ADHESION PROMOTER AND WETTING AGENT

BACKGROUND OF THE INVENTION

[0001]

The present invention is related to materials for promoting adhesion, and more particularly materials and methods for increasing adhesion of a siloxane-type (or other hybrid organic-inorganic metal oxide type) material to another layer/material or a subsrate.

[0002]

Conventional primers are typically monolayers. The materials category in this invention can be applied either as monolayers or nm-thick films. This is advantageous if complex surfaces are coated.

[0003]

Conventional adhesion promoters and wetting agents are based on the non-area-selective chemical reactions, meaning that the material can be lithographically patterned.

SUMMARY OF THE INVENTION

[0004]

The present invention is directed to a novel material to be used for the improvement of siloxane based materials adhesion to various substrate materials, optical material layers (so called buffer and cladding), metal or semiconductor materials and dielectrics. The material also improves the wetting properties of liquid phase deposited optical and dielectric materials. The adhesion promoting material of the invention is particularly well suited to improve the adhesion between fluorinated (hydrophobic) surfaces, i.e. partially or per-fluorinated. In addition, one special property of the

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material is that it may improve lithographic processing capabilities due to its photosensitivity.

[0005]

The adhesion promoting materials of the invention can: 1) improve adhesion of spin-on siloxane film to the to layer underneath of that, 2) improve wetting of perfluorinated (also partially fluorinated and non-fluorinated applies) siloxane material to the other surface, which may also be fluorinated or hydrophobic, and/or 3) eliminate/minimize the development residual to stick to a waveguide structure or buffer layer/substrate.

[0006]

Various combinations of silanes, such as described below, can be used for the adhesion promoter material. Preferred precursors comprise silane precursors with cross linking capability (e.g. epoxy, alkenyl, etc. moieties) and silane precursors with alkyl or aryl groups. The silane precursors need not be fluorinated.

[0007]

In one embodiment of the invention, an inorganically cross linked material (hydrolyzed/condensed materials) is deposited as an adhesion promoter on a substrate (or other article or layer) followed by a similar organically cross linked material (hydrolyzed/condensed materials), where the two materials are the same, except the adhesion promoter is applied as part of a very dilute solution. In another embodiment of the invention, the adhesion promoter is similar to the later applied material, except that the amount of fluorination is less than in the later applied layer. In yet another embodiment of the invention, the precursors and/or ratios of precursors are different between the adhesion

promoter and the next applied layer. And in a still further embodiment of the invention, a plurality of adhesion promoter layers are applied. And in yet another embodiment, a plurality of adhesion promoter layers are applied, wherein later applied layer(s) are more fluorinated than earlier applied layers.

[0008]

The materials compositions can be tuned at molecular or organo-moiety so that the materials surface energy changes as a function of the composite concentration.
Also, the surface energy can also be changed gradually by applying layered thin films with different materials compositions.

[0009]

Furthermore, adhesion promoters optical properties can be changed at selected wavelength so that the thin film can be fully transparent, semitransparent or opaque.

[0010]

Material coating categories include:

1) Monomeric layer
2) A layer based on oligomeric or small molecular weight material, and
3) A layer based on polymer or high molecular weight material.

[0011]

Uniquely, the adhesion promoter is tailored to be totally compatible with the top layer, and the solvent system used for both the layers are the same - this reduces the possibility of polarity mismatch seen in conventional systems.

[0012]

Additionally, the reactive groups (silanols being an example) for the layers can be the same and the chain polarity of internal polarization can be controlled by using fluorinated or aromatic layers in one or the other. For example in a waveguide application example, the bottom layer can be non fluorinated while the top layer is a F based system for controlling optical attenuation etc.

[0013]

Additionally, one of the problems in adhesion promoting layers is the inability of lithographic processes (such as exposure/development, etching etc) to clean the layers completely (usually in the IC industry an additional step such as aching is required to remove the crosslinked adhesion layers).

[0014]

Additionally, adhesion improvement is not limited to monolayers (or at best a few layers) and the invention builds strong adhesive interface as well a cohesive build up of subsequent layers.

[0015]

The properties desired in the film can be optical, mechanical (modulus etc) for applications in the IC areas (IM and IL dielectrics).

[0016]

Hydrophobicity of the layer can be easily controlled by the combination of precursors listed - controlling this is a problem in the industry today as lithographic developers range from totally polar aqueous to nonpolar systems. Model

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compounds listed here can be modified to attain different interfacial energy levels.

[0017]

It is also implied that Silanol based adhesion promoters can be used on a variety of surfaces - (Si, Oxide, Nitride, metals (Al, Cu,Mo,W)) with no interfacial failure using conventional tests (scotch tape peel tests etc).

[0018]

Additionally, the use of the diluted polymer solution has a wetting effect as the siloxane based systems tend to be difficult to spread on wafers and the plasticizing effect allows these materials to be used as wetting agents for these systems.

[0019]

The present invention is directed to a method for forming a hybrid organic inorganic layer (as an adhesion promoter) by: hydrolyzing a silane selected from the group consisting of a tetraalkoxysilane, a trialkoxysilane, a trichlorosilane, a dialkoxysilane, and a dichlorosilane, with a compound of the general formula: $R^1R^2R^4MR^5$, wherein R^1, R^2 and R^4 are independently an aryl, alkyl, alkenyl, epoxy or alkynyl group, wherein at least one of R^1, R^2 and R^4 is fully or partially fluorinated, wherein M is selected from group IV of the periodic table, and wherein R^5 is either an alkoxy group, OR^3, or a halogen, X - followed by depositing the material on the substrate.

[0020]

In various embodiments, OR^3 can have one to 10 carbons, one to 7 carbons, and more preferably one to five carbons, and the like.

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[0021]

In another embodiment of the present invention a compound of the general formula $R^1_{4-m}SiOR^3_m$ wherein m is an integer from 2 to 4, OR^3 is an alkoxy, acyl or acyloxy group, is reacted with a compound of the general formula R^2X^2 + Mg, wherein X^2 is Br or I; where R^1 and R^2 are independently selected from alkyl, alkenyl, aryl, alkynyl or epoxy, and at least one of R^1 and R^2 is partially or fully fluorinated to form Fluorinated compositions.

[0022]

A coating compound is made of the general formula $R^2R^{IV}_{-m}SiOR^3_{m-1}$ with a molecular weight between 3000 and 100,000. This is then followed by reacting $R^2R^{IV}_{-m}SiOR^3_{m-1}$ with a halogen or halogen compound in order to replace one or more OR^3 groups with a halogen. This reaction forms $R^2R^{IV}_{-m}SiOR^3_{m-1-n}X_n$, where X is a halogen and n is from 1 to 3 and m > n, except where R^1 is fluorinated phenyl and OR^3 is ethoxy. A lower molecular weight, or monomers of the above, are preferred and combinations of these can be used as adhesion promoters. Generally adhesion promoters are used as dilute solutions to cover the substrate without any wetting problems.

[0023]

Choice of the terminal groups (Chloro, alkoxy or acetoxy) is determined by the surface energy requirements of the surface. The pendant groups R1 -R4 are chosen to modify the terminal surface energies as required by subsequent processing. For example Fluorinated substituents are preferred for hydrophobic systems while long chain non fluorinated groups offer monolayer capabilities. This invention extends conventional adhesion promotion to possible cohesion enhancements by using materials and prepolymers of the same

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material as the adhesion promoter or side chain modified materials compatible with the initial layers.

[0024]

There are many different silicon compounds suitable for use in the present invention. Preferred are those that are fluorinated, preferably perfluorinated – or, where multiple different silicon compounds are used, where at least one of the compounds is fluorinated, preferably perfluorinated – and more preferably, when multiple different silicon compounds are used, all are at least partially fluorinated or even all perfluorinated.

[0025]

In this section, compounds are described that can be hydrolyzed and condensed (alone or with one or more other compounds) into a hybrid organic-inorganic anti-stiction material having a molecular weight of from 500 to 100,000. The molecular weight can be in the lower end of this range (e.g., from 500 to 5,000, or more preferably 500 to 3,000) or the anti-stiction material can have a molecular weight in the upper end of this range (such as from 5,000 to 100,000 or from 10,000 to 50,000). In addition, it may be desirable to mix an anti-stiction material having a lower molecular weight with an anti-stiction material having a higher molecular weight. The anti-stiction material can be suitably deposited such as by spin-on, spray coating, dip coating, or the like. Such compounds are preferably partially or fully fluorinated, though not necessarily so. The compounds will preferably have an element M selected from groups 3-6 or 13-16 of the periodic table, which element is preferably tetra-valent, such as those elements selected from group IV of the periodic table. Connected to this element M are four substituents (if tetra-valent), wherein from one to three of these substituents are

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organic groups to be discussed further below, with the remainder being a halogen, alkoxy, acyl, acyloxy or -OH group.

BRIEF DESCRIPTION OF THE DRAWING

[0026]

Fig. 1 shows the structure of an embodiment of the hybrid organic-inorganic adhesion promoter of the present invention.

DETAILED DESCRIPTION

[0027]

In this section, compounds are described that can be hydrolyzed and condensed (alone or with one or more other compounds) into a hybrid material having a molecular weight of from 500 to 100,000 (preferably from 500 to 5000, or more preferably 500 to 3000), which material can be deposited by spin-on, spray coating, dip coating, or the like. Such compounds are preferably partially or fully fluorinated, though not necessarily so. The compounds will preferably have an element M selected from groups 3-6 or 13-16 of the periodic table, which element is preferably tri-, tetra- or penta-valent, and more preferably tetravalent, such as those elements selected from group 14 of the periodic table. Connected to this element M are from three to five substituents, wherein from one to three of these substituents are organic groups to be discussed further below, with the remainder being a halogen or an alkoxy group.

[0028]

Compound Example I:

A compound is provided of the general formula: $R^1MOR^3_3$, where R^1 is any partially or fully fluorinated organic group (preferably a partially or fully fluorinated aryl, alkenyl, alkynyl or alkyl group), where M is an element selected from column 14 of the periodic table, and where OR^3 is an alkoxy

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group – except where M is Si, R^1 is perfluorinated phenyl or perfluorinated vinyl, and OR^3 is ethoxy, which, though not novel per se, can be part of one of the novel methods for making the materials of the invention as will be discussed further below. R^1 can have an inorganic component, though if so, a portion should preferably be a partially or fully fluorinated organic component. In a more preferred example of this, R^1 comprises a double bond that is capable of physical alteration or degradation in the presence of an electron beam, or electromagnetic radiation and a photoinitiator (or sensitizer, photoacid or thermal initiator - to be discussed further below). In this example, R^1 could be an alkenyl group such as a vinyl group, or could be an epoxy or acrylate group, that is preferably partially or fully fluorinated. Such a group, as will be discussed further herein, can allow for crosslinking upon application of an electron beam or preferably electromagnetic radiation (e.g. directing ultraviolet light through a mask with the material comprising a photoinitiator). In the alternative, R^1 could be an organic group that is (or a hybrid organic-inorganic group that comprises) a single or multi ring structure (an "aryl group") or an alkyl group of any length, such as from 1 to 14 carbon atoms or longer (preferably 4-10) – the alkyl group capable of being a straight or branched chain. If R^1 is a ring structure, or a carbon chain of sufficient length (e.g. 4 (or 5) or more carbons), then such an R^1 group can provide bulk to the final material once hydrolyzed, condensed and deposited on a substrate. If R^1 is a ring structure, whether single ring or multi ring, it can have substituents thereon, fluorinated, though not necessarily, such as alkyl or alkenyl substituents (preferably from 1 to 5 carbons), and where the substituents on the ring structure can be at from 1 to 3 locations around the ring. R^1 can be a 4 to 8 sided ring structure (preferably 5 or 6 sided) which ring structure could comprise N or O. R1

could comprise nitrogen, or R^1 can also have an oxygen component, such as a carboxylate group (e.g. acrylate, butenecarboxylate, propenecarboxylate, etc.).

[0029]

In the example above, in R^{1}MOR$^3{}_3$, M can be a tetravalent element from column 14 of the periodic table (e.g. Si or Ge), or a tetravalent element from column 16 – e.g. Se (or a tetravalent early transition metal – such as titanium or zirconium). Also, OR^3 is an alkoxy group, though preferably one having from 1 to 4 carbon atoms (longer alkoxy groups can be used, but are more expensive). Specific examples include:
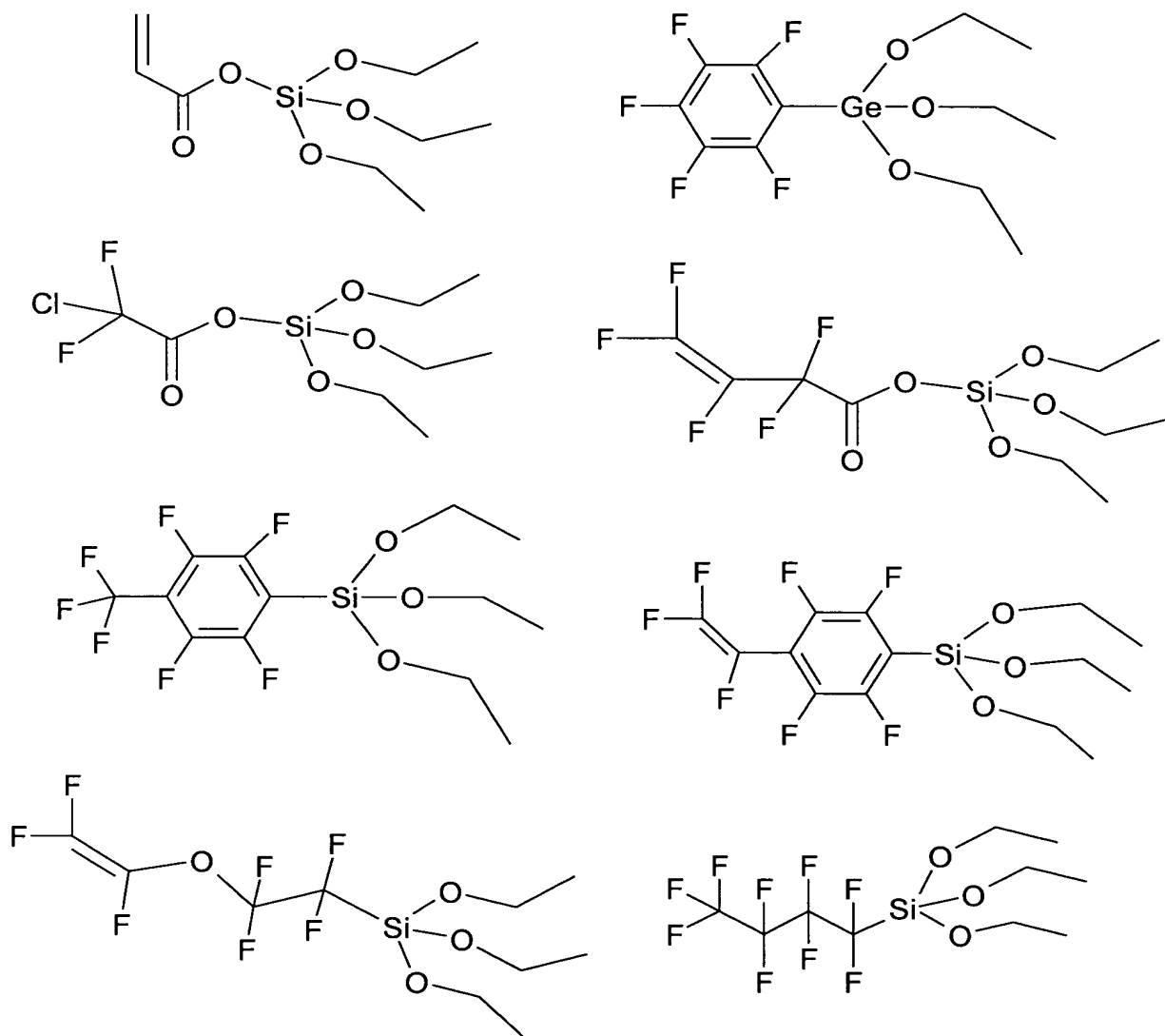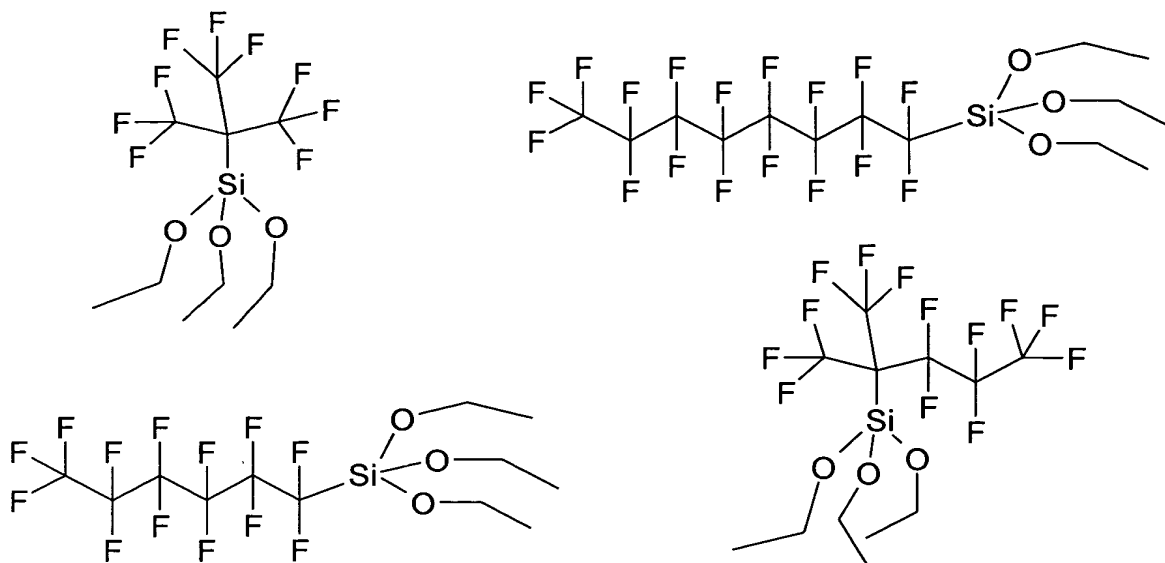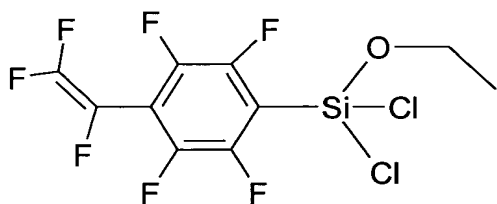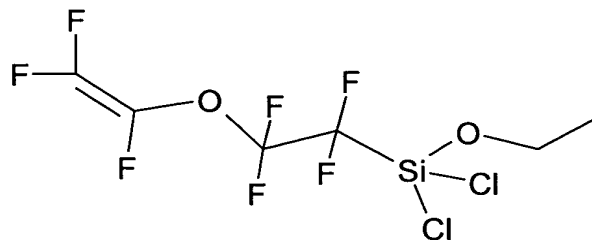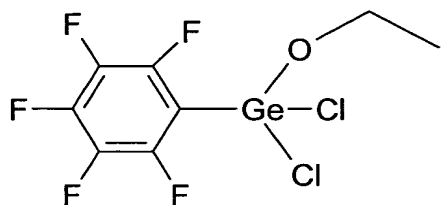
[0030]

Compound Example II:

In yet another compound example, a compound is provided of the general formula: $R^1MOR^3_2X$, where R^1 is any partially or fully fluorinated organic group (preferably a partially or fully fluorinated aryl, alkenyl, alkynyl or alkyl group) as set forth above, where M is an element selected from group 14 of the periodic table as mentioned above, where X is a halogen, and where OR^3 is an alkoxy group as above. X in this example is preferably F, Cl, Br or I, and more preferably Cl or Br. Specific examples of compounds within this category include:

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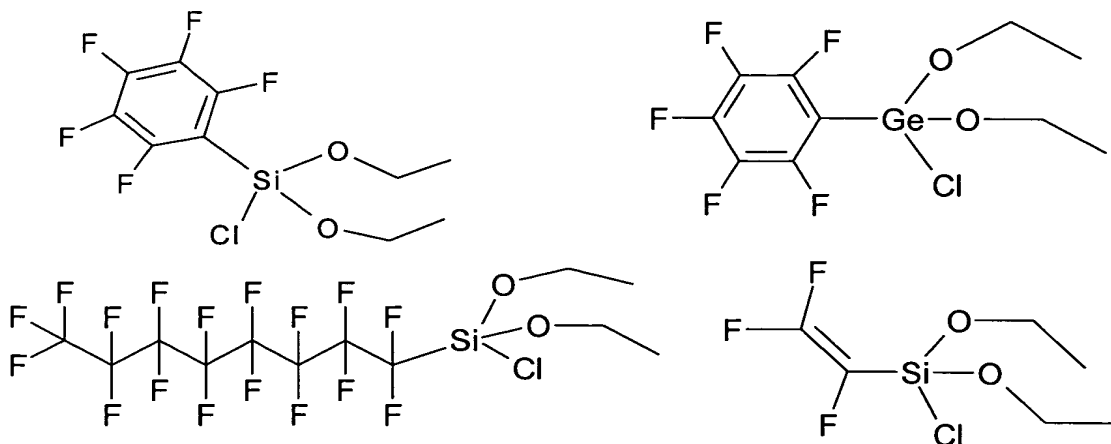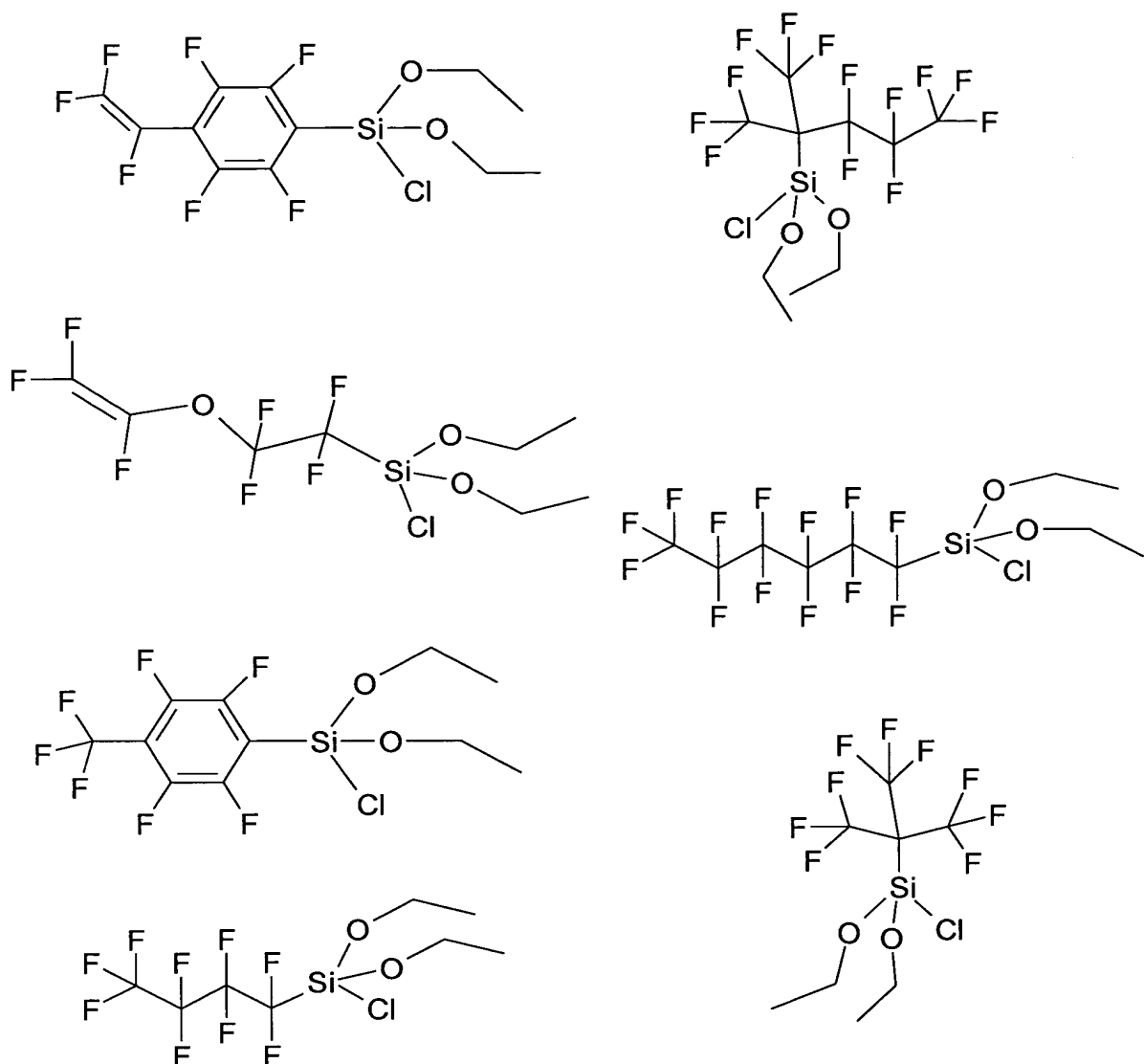
[0031]

Compound Example III:

In another compound example, a compound is provided of the general formula: $R^1MX_2OR^3$, where R^1 is any partially or fully fluorinated organic group (preferably a partially or fully fluorinated aryl, alkenyl, alkynyl or alkyl group) as set forth above, where M is an element selected from group 14 of the periodic table as mentioned above, where OR^3 is an alkoxy group as above, and where X is a halogen as above – Except where M is Si, R^1 is perfluorinated phenyl, X is Cl, and

OR³ is ethoxy, which, though not novel per se, is novel when used as part of the methods for making the materials of the invention as will be discussed further below. Specific examples within this category include:
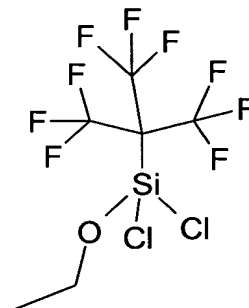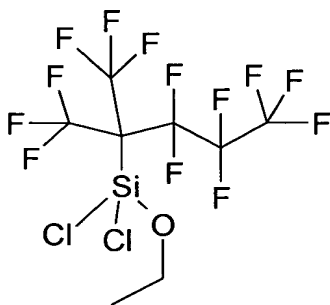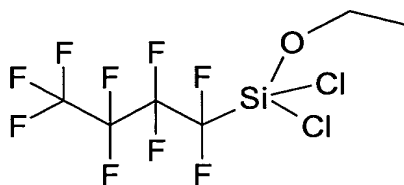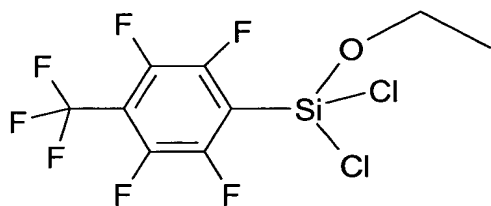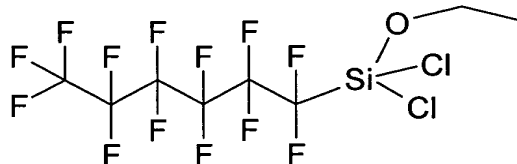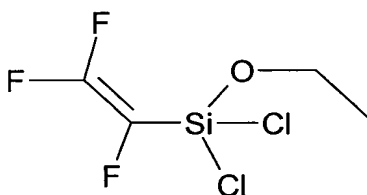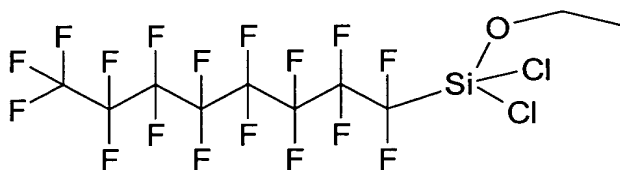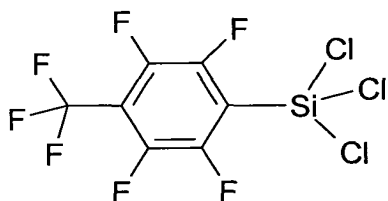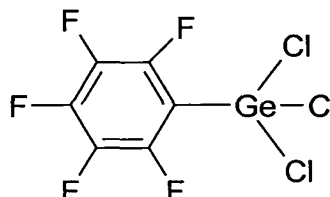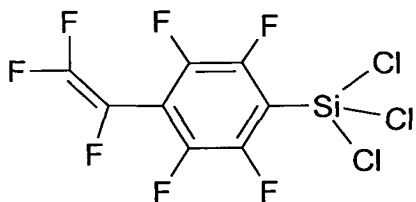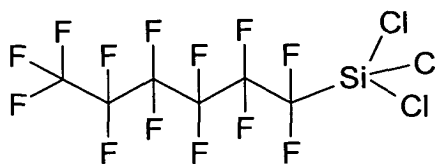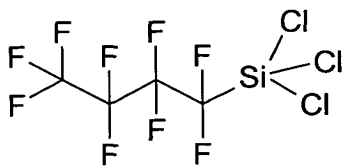
[0032]

Compound Example IV:

In a further compound example, a compound is provided of the general formula: R^1MX_3, where R^1 is any partially or fully fluorinated organic group (preferably a partially or fully fluorinated aryl, alkenyl, alkynyl or alkyl group) as set forth above, where M is an element selected from group 14 of the periodic table as mentioned above, and where X is a halogen as above - Except where M is Si, R^1 is perfluorinated phenyl, perfluorinated methyl or perfluorinated vinyl, and X is Cl, which, though not novel per se, are novel when used as part of the methods for making the materials of the invention as will be discussed further below. (If M is Si and X is Cl, some of these novel trichlorosilanes could be used for forming self assembled monolayers for making a surface hydrophobic, preferably by application in the vapor phase to a surface made of silicon and having OH end groups and moisture.) Specific examples within this category include:
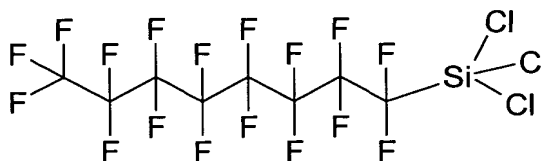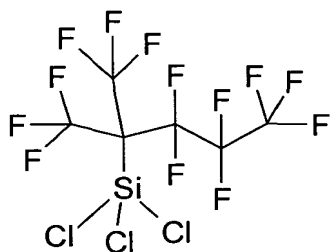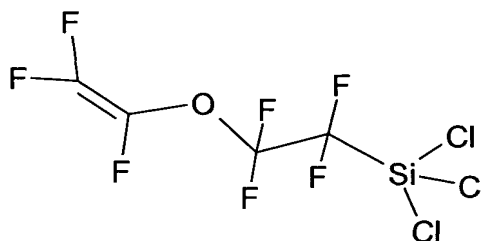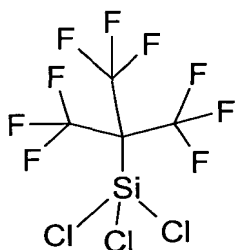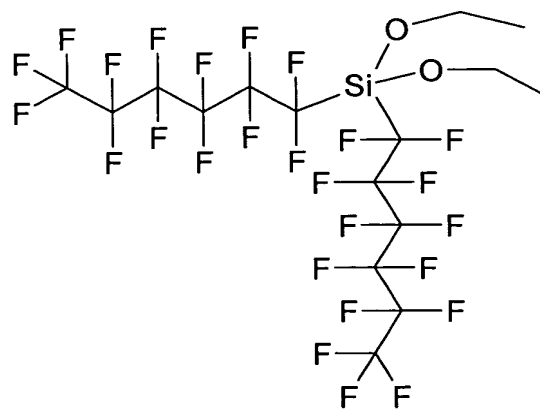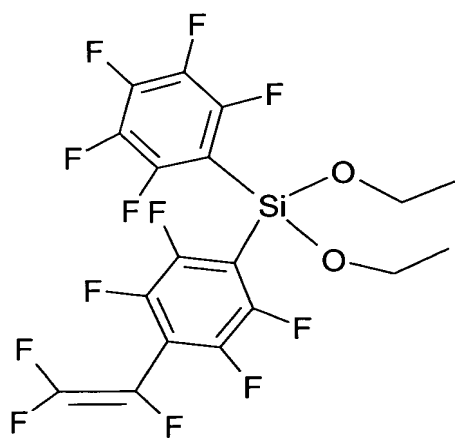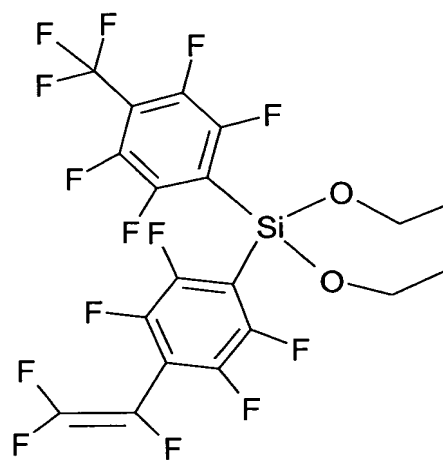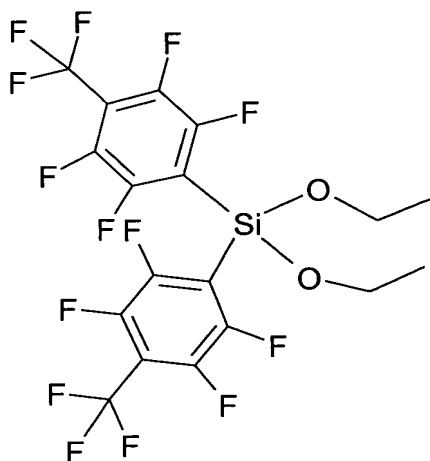
[0033]

Compound Example V:

In yet another compound example, a compound is provided of the general formula: $R^1R^2MOR^3{}_2$, where R^1 is any partially or fully fluorinated organic group (preferably a partially or fully fluorinated aryl, alkenyl, alkynyl or alkyl group) as set forth above with respect to R^1, R^2 is any partially or fully fluorinated organic group (preferably a partially or fully fluorinated aryl, alkenyl, alkynyl or alkyl group) as set forth above with respect to R^1, or any such organic groups nonfluorinated, and where R^1 and R^2 are the same or different from each other, where M is an element selected from group 14 of the periodic table as mentioned above, and where OR^3 is an alkoxy group as above -- exce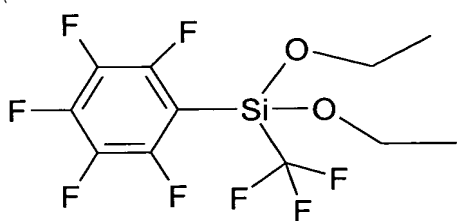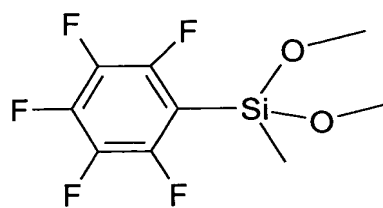pt where M is Si, OR^3 is ethoxy and R^1 and R^2 are perfluorinated phenyl groups, which compound is not novel per se, but is novel when used as part of the methods for making materials of the invention as set forth below. Specific examples within this category include:
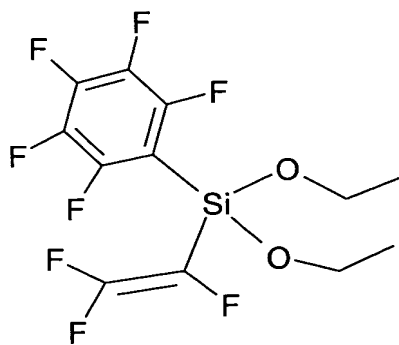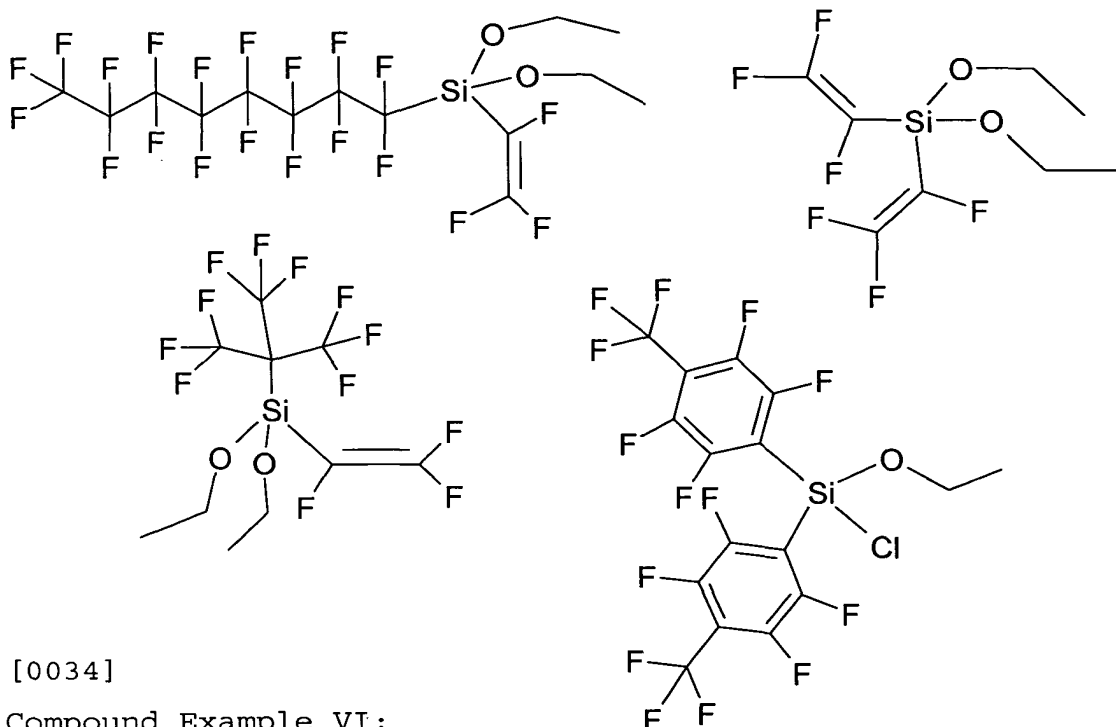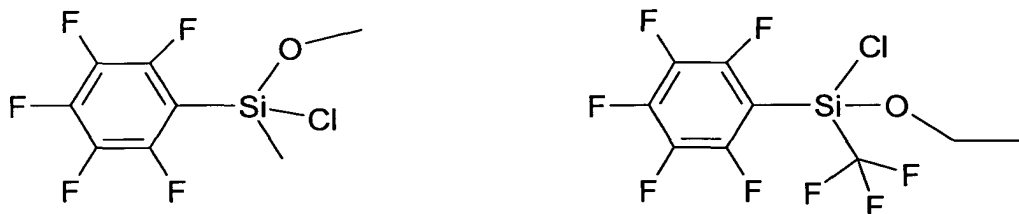
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[0034]

Compound Example VI:
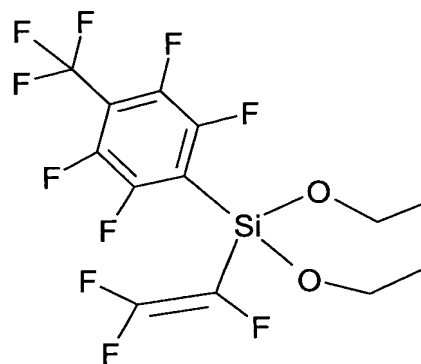
In another compound example, a compound is provided of the general formula: $R^1R^2MXOR^3$, where R^1 is any partially or fully fluorinated organic group (preferably a partially or fully fluorinated aryl, alkenyl, alkynyl or alkyl group) as set forth above with respect to R^1, R^2 is any partially or fully fluorinated organic group (preferably a partially or fully fluorinated aryl, alkenyl, alkynyl or alkyl group) as set forth above with respect to R^1, or any such organic groups nonfluorinated, and where R^1 and R^2 are the same or different from each other, where M is an element selected from group 14 of the periodic table as mentioned above, where OR^3 is an alkoxy group as above, and where X is a halogen. R^1 and R^2 can be the same or different from each other. Specific examples within this category include:

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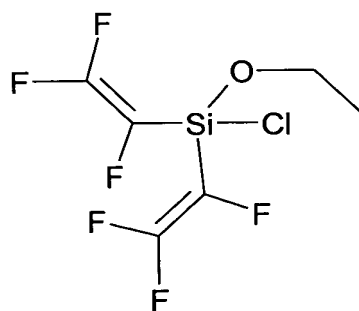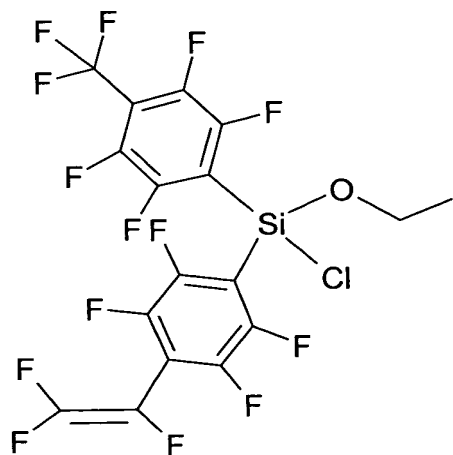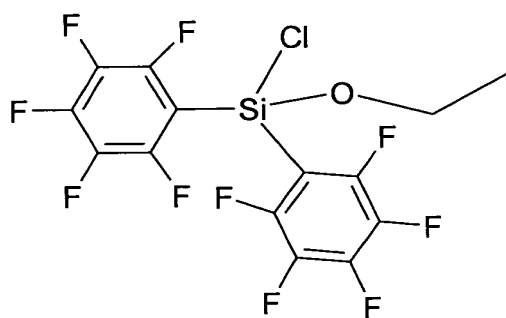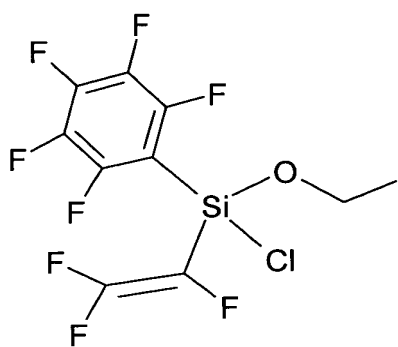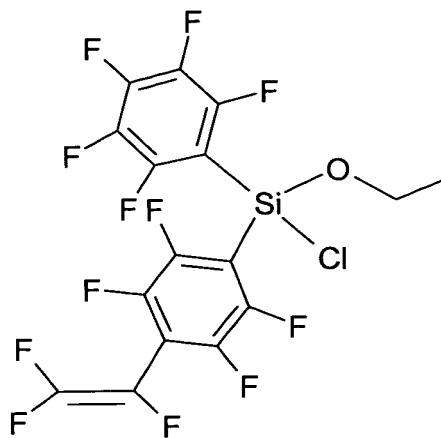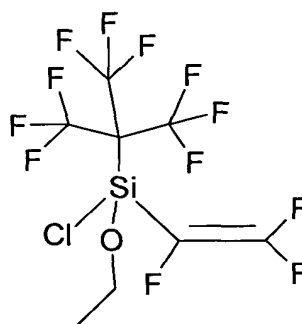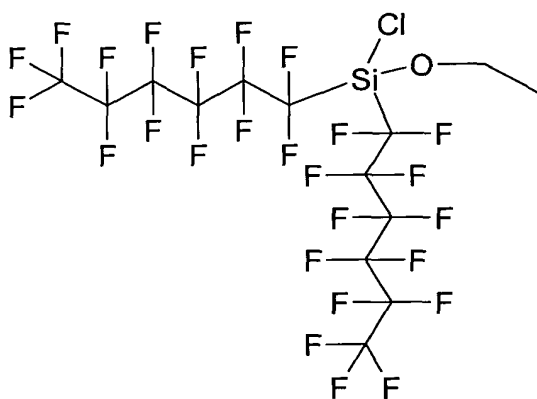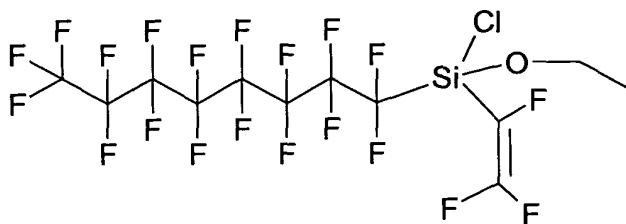
[0035]

Compound Example VII:

In a further compound example, a compound is provided of the general formula: $R^1 R^2 MX_2$, where R^1 is any partially or fully fluorinated organic group (preferably a partially or fully fluorinated aryl, alkenyl, alkynyl or alkyl group) as set forth above with respect to R^1, R^2 is any partially or fully fluorinated organic group (preferably a partially or fully fluorinated aryl, alkenyl, alkynyl or alkyl group) as set forth above with respect to R^1, or any such organic groups nonfluorinated, and where R^1 and R^2 are the same or different from each other, where M is an element selected from group 14 of the periodic table as mentioned above, and where X is a halogen as above - Except where M is Si, R^1 and R^2 are perfluorinated phenyl, and X is Cl, which, though not novel

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per se, is novel when used as part of the methods for making the materials of the invention as will be discussed further below. Specific examples within this category include:
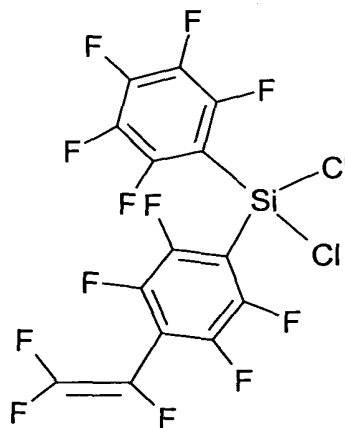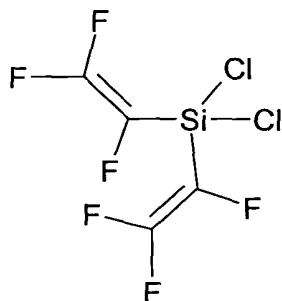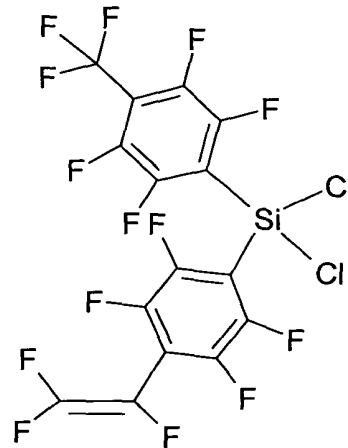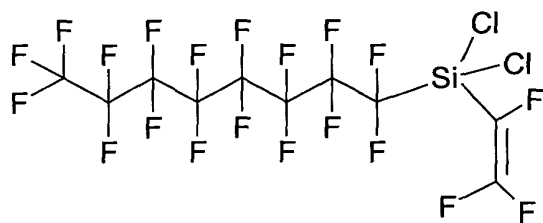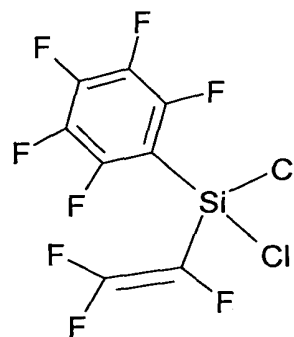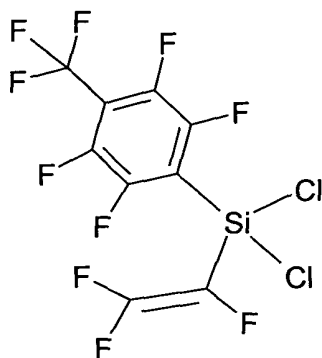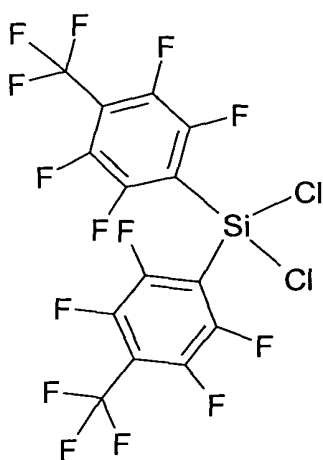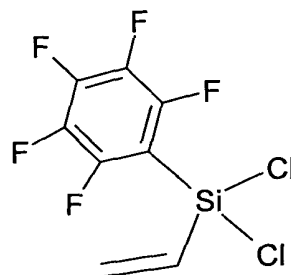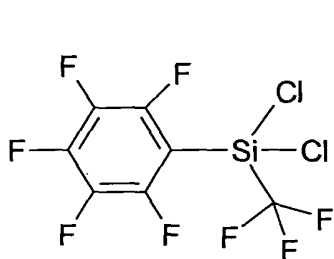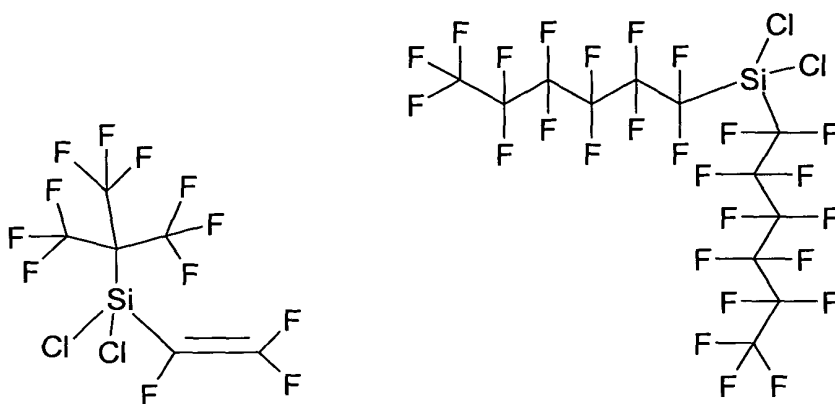
As Compounds V-VII have two organic groups, they can be formed by various combinations of Methods A, B and/or C (described in further detail below).
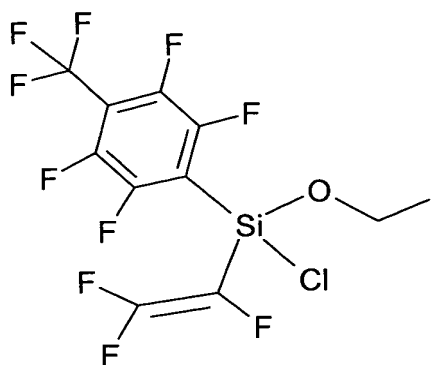
[0036]

Compound VIII:

In a further compound example, a compound is provided of the general formula: $R^1R^2\,R^3MOR^3$, where R^1, R^2 and R^3 are independently an aryl, alkenyl, alkynyl or alkyl group) as set forth above with respect to R^1 and R^2, and where R^1, R^2 and R^3 can each be the same or different from each other (and preferably at least one of where R^1, R^2 and R^3 is partially or fully fluorinated), where M is preferably an element selected from group 14 of the periodic table as above, and where OR^3 is an alkoxy group as above. One example is:

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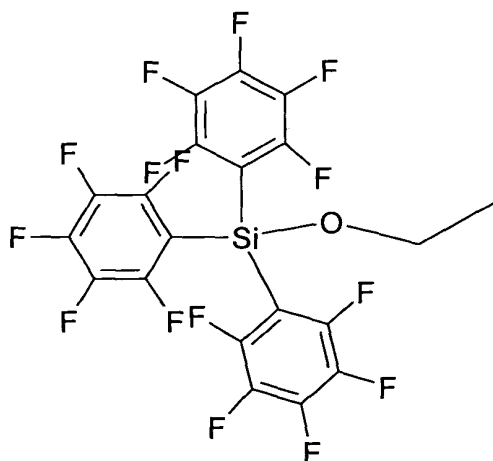
though the organic groups need not each be the same as in this example, and need not each be fluorinated (though preferably at least one of the organic groups is fluorinated).

[0037]
Compound IX:

In another compound example, a compound is provided of the general formula: R^1R^2 R^3MX, where R^1, R^2 and R^3 are independently an aryl, alkenyl, alkynyl or alkyl group) as set forth above with respect to R^1 and R^2, and where R^1, R^2 and R^3 can each be the same or different from each other (and preferably at least one of where R^1, R^2 and R^3 is partially or fully fluorinated), where M is preferably an element selected from group 14 of the periodic table as above, and where X is a halogen as above. One example is:
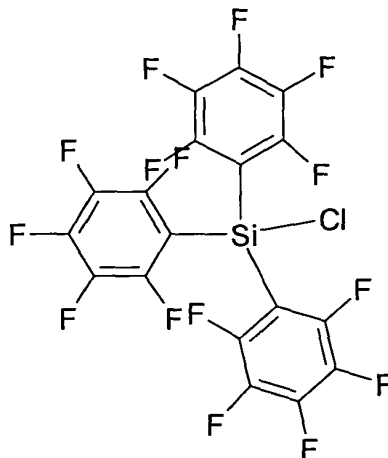
As Compounds VIII and IX have three organic groups, they can be formed by various combinations of Methods A, B and/or C (which methods are described in further detail below).

[0038]
Other Compounds:

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Additional compounds for making the materials of the invention include those having the general formula R^1MHX_2 where R^1, M and X are as above and H is hydrogen. One example is:
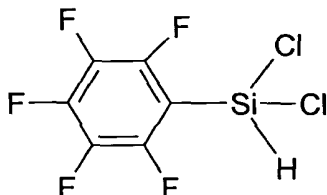
Other examples, where the fluorinated phenyl group is replaced with a substituted phenyl, fluorinated alkyl, vinyl, etc. are possible.

[0039]

It should be noted that M in the compound formula examples above need not be tetravalent. M can also have other valencies, though preferably tri- or penta-valent. Examples would include early transition metals in group 3 or 5 of the periodic table (e.g. Y, V or Ta), or elements in columns 13 (column headed by B) or 15 (column headed by N), such as B, Al or As. In such situations, the compounds above would have one fewer or one additional alkoxy (OR^3), halogen (X) or an organic group (R^1 or R^2 independently from the other organic group(s)). Examples include R^1MOR^3X, $R^1MOR^3_2$, R^1MX_2, R^1R^2MX, $R^1R^2MOR^3$, where M is a trivalent early transition metal (or similar examples with five substituents selected from R^1 and/or R^2 groups, as well as alkoxy and halogen groups for pentavalent elements (including metalloids or transition metals). Such compounds could have the formula $R1_{3-m}MOR3_m$, $R1_{5-m}MOR3_m$, $R2R1_{4-m}MOR3_m$ or $R2R1_{4-m}MOR3_m$. If such tri- or penta-valent elements are used, such a compound would preferably be hydrolyzed and condensed as a dopant, rather than as the main portion of the material at the time of hydrolysis and condensation (likewise with non-silicon tetravalent elements that form compounds in accordance

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with the tetravalent examples above, such as germanium compounds).

[0040]

It should also be noted that the structures illustrated above are exemplary only, as other ring structures (3 sided – e.g. epoxy, or 4 to 8 sided – preferably 5 or 6 sided) are possible, which structures can include nitrogen or oxygen in or bound the ring. The aryl group can have from 1 to 3 substitutents, such as one or more methyl, ethyl, ally, vinyl or other substituents – that can be fluorinated or not. Also, carbon chain R groups can include oxygen (e.g. carboxylate) or nitrogen, or sulpher. If an alkyl group is bound to the silicon (or other M group), it can have from 1 to 4 carbons (e.g. a C2+ straight or C3+ branched chain), or up to 14 carbons (or more) – if used as a bulk enhancing group for later hydrolysis and deposition, 4 or more carbons are preferable. These aryl groups can be fully or partially fluorinated, as can alkenyl or alkynyl groups if used.

METHODS OF MAKING THE COMPOUNDS FOR LATER HYDROLYSIS AND CONDENSATION

[0041]

In a number of the following examples of methods for making the materials of the invention, "M" is silicon, OR^3 is ethoxy, and X is Cl. However, as noted above, other alkoxy groups could easily be used (methoxy, propoxy, etc.), and other group 3-5 or 13-16 elements could be used in place of silicon and other halogens in place of chlorine. Starting materials can vary from tetraethoxy silane, to ethoxy silanes having one or more organic groups bound to the silicon, to chorosilanes having one or more chlorine groups and/or one or more organic groups, as well as starting materials having

chlorine and alkoxy groups and with one or more organic groups. Any compound examples within Compounds I-IX above could be used as starting materials - or could be intermediate or final compounds as will be seen below. For example, trifluorovinyltriethoxysilane could be a final compound resulting from reacting a particular trifluorovinyl compound with tetraethoxysilane, or trifluorovinylsilane could be a starting material that, when reacted with a particular pentafluorophenyl compound, results in pentafluorophenyltrifluorovinyldiethoxysilane. As mentioned above, it is also preferred that any organic groups that are part of the starting material or are "added" by chemical reaction to become part of the compound as set forth below, are partially or fully fluorinated (or fully or partially deuterated), though such is not necessary as will also be seen below.

[0042]

One example of a method for making the materials of the present invention comprises providing a compound R^1_{4-q} MOR^3_q where M is selected from group 14 of the periodic table, OR^3 is an alkoxy group, R^1 is an alkyl, alkenyl, aryl or alkynyl, and q is from 2 to 4; reacting the compound R^1_{4-q} MOR^3_q with either a) Mg and R^2X^2 where X^2 is Cl, Br or I and R^2 is an alkyl, alkenyl, aryl or alkynyl group, or b) reacting with R^2X^1 where R^2 is an alkyl, alkenyl, aryl or alkynyl group and wherein R^2 is fully or partially fluorinated or deuterated and X^1 is an element from group 1 of the periodic table; so as to replace one of the OR^3 groups in R^1_{4-q} MOR^3_q so as to form R^1_{4-q} $R^2MOR^3_{q-1}$.

[0043]

The starting material preferably has 1 or 2 (or no) organic groups (R^1) bound to the group 14 element "M", which

organic groups may or may not comprise fluorine, with the remaining groups bound to M being alkoxy groups. An additional preferably fluorinated (partially of fully) organic group becomes bound to the group 14 element by one of a number of reactions. One method (Method A) involves reacting the starting material with magnesium and a compound having the desired organic group (R^2) bound to a halogen X^2 (preferably Cl, Br or I) – namely $R^2 X^2$, which reaction replaces one of the alkoxy groups with the organic group R^2. In the above example, a single alkoxy group is replaced, however, depending upon the molar ratios of starting material to R^2X^2 and Mg, more than one alkoxy group can be replaced with an R^2 organic group. In one example of the above, a tetraethoxysilane, MOR^3_4 is reacted with a compound R^2X^2 where R^2 is a preferably fluorinated alkyl, aryl, alkenyl or alkynyl group and X^2 is preferably Br or I, so as to form $R^2MOR^3_3$. In another example, $R^1MOR^3_3$ is reacted with R^2X^2 so as to form $R^1R^2MOR^3_2$. This group of reactions can be referred to as: reacting the starting material $R^1_{4-q} MOR^3_q$ with R^2X^2 where R^2 is a preferably fluorinated alkyl, aryl, alkenyl or alkynyl group and X^2 is preferably Br or I, so as to form $R^1_{4-q} R^2MOR^3_{q-1}$.

[0044]

This method A can be described as a method comprising reacting a compound of the general formula $R^1_{4-m}MOR^3_m$, wherein m is an integer from 2 to 4, OR^3 is an alkoxy, and M is an element selected from group 14 of the periodic table; with a compound of the general formula R^2X^2 + Mg, wherein X^2 is Br or I, where R^1 and R^2 are independently selected from alkyl, alkenyl, aryl or alkynyl, and wherein at least one of R^1 and R^2 is partially or fully fluorinated, so as to make a compound of the general formula $R^2MR^1_{3-n}OR^3_n$, wherein n is an integer from 1 to 3.

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[0045]

An alternate to the above method (Method B) is to react the same starting materials ($R^1_{4-q} MOR^3_q$) with a compound R^2X^1 where, as above, R^2 is an alkyl, alkenyl, aryl or alkynyl group and wherein R^2 is fully or partially fluorinated or deuterated and X^1 is an element from group 1 of the periodic table; so as to replace an OR^3 group in $R^1_{4-q} MOR^3_q$ to form $R^1_{4-q} R^2MOR^3_{q-1}$. In this example, X^1 is an element from group 1 of the periodic table, and is preferably Na, Li or K (more preferably Na or Li). In one example of the above, a tetraethoxysilane, MOR^3_4 is reacted with a compound R^2X^1 where R^2 is a preferably fluorinated alkyl, aryl, alkenyl or alkynyl group and X^1 is preferably an element from group I of the periodic table, so as to form $R^2MOR^3_3$. In another example, $R^1MOR^3_3$ is reacted with R^2X^1 so as to form $R^1R^2MOR^3_2$.

[0046]

This method B can be described as a method comprising reacting a compound of the general formula $R1_{4-m}MOR3_m$ wherein m is an integer from 2 to 4, R1 is selected from alkyl, alkenyl, aryl, or alkyl, alkenyl or aryl, and wherein R1 is nonfluorinated, or fully or partially fluorinated, OR3 is alkoxy, and M is an element selected from group 14 of the periodic table; with a compound of the general formula R2M1, wherein R2 is selected from alkyl, alkenyl, aryl, alkynyl, and wherein R2 is at least partially fluorinated; and M1 is an element from group I of the periodic table; so as to make a compound of the general formula $R1_{4-m}MOR3_{m-1}R2$.

[0047]

A modification (Method C) of the aforementioned (Method B), is to react the starting material ($R^1_{4-q} MOR^3_q$) with a halogen or halogen compound so as to replace one or more of the OR^3 groups with a halogen group due to reaction with the

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halogen or halogen compound. The halogen or halogen compound can be any suitable material such as hydrobromic acid, thionylbromide, hydrochloric acid, chlorine, bromine, thionylchloride or sulfurylchloride and the like. Depending upon the ratio of halogen or halogen compound to starting material (and other parameters such as reaction time and/or temperature), one or more alkoxy groups can be replaced by a halogen group – though in most examples, a single alkoxy group or all alkoxy groups will be replaced. If a single alkoxy group is replaced, then the starting material R^1_{4-q} MOR^3_q becomes R^1_{4-q} $MOR^3_{q-1}X^3$ where X^3 is a halogen from the halogen or halogen compound reacted with the starting material (or simply begin with starting material R^1_{4-q} $MOR^3_{q-1}X^3$). If all alkoxy groups are replaced due to the reaction with the halogen or halogen compound, then the starting material R^1_{4-q} MOR^3_q becomes R^1_{4-q} MX^3_q. Then, as mentioned for Method B above, either starting material R^1_{4-q} $MOR^3_{q-1}X^3$ or R^1_{4-q} MX^3_q is reacted with a compound R^2X^1 where R^2 is a preferably fluorinated alkyl, aryl, alkenyl or alkynyl group and X^1 is preferably an element from group I of the periodic table, so as to form R^1_{4-q} $R^2MOR^3_{q-1}$, $R^1_{4-q}R^2MX^3_{q-1}$ (or even $R^1_{4-q}R^2_2$ MX^3_{q-2} depending upon reaction conditions). A reaction with R^1_{4-q} $MOR^3_{q-1}X^3$ is preferred due to greater ease of control of the reaction.

[0048]

This Method C can be described as a method comprising reacting a compound of the general formula X3MOR3$_3$, where X3 is a halogen, M is an element selected from group 14 of the periodic table, and OR3 is alkoxy; with a compound of the general formula R1M1; where R1 is selected from alkyl, alkenyl, aryl and alkynyl and wherein R1 is partially or fully fluorinated; and M1 is an element from group I of the periodic table; so as to form a compound of the general formula R1MOR3$_3$.

[0049]

Related Methods B and C can be described as a single method comprising reacting a compound of the general formula $R1_{4-m}MOR3_{m-n}X_n$ wherein m is an integer from 2 to 4, and n is an integer from 0 to 2, R1 is selected from alkyl, alkenyl, aryl, or alkyl, alkenyl or aryl, and wherein R1 is nonfluorinated, or fully or partially fluorinated; OR3 is alkoxy, and M is an element selected from group 14 of the periodic table; with a compound of the general formula R2M1, wherein R2 is selected from alkyl, alkenyl, aryl, alkynyl, and wherein R2 is at least partially fluorinated, and M1 is an element from group I of the periodic table; so as to make a compound of the general formula $R2MR1_{4-m}OR3_{m-n}X_{n-1}$.

[0050]

Of course, as will be seen below, the above starting materials in the method examples set forth above are only examples, as many other starting materials could be used. For example, the starting material could be a halide rather than an alkoxide (e.g. a mono-, di- or trichlorosilanes) or another material having both alkoxy and halogen groups on the group 14 element, along with 0, 1 or even 2 organic groups (alkyl, alkenyl, aryl, alkynyl) also bound to the group 14 element. Though the methods for making the materials of the invention preferably use starting materials having the group 14 element set forth above, many different combinations of alkoxy groups, halogen groups, and organic groups (alkyl, alkenyl,…etc.) can be bound to the group 14 element. And, of course, such starting materials can be commercially available starting materials or can be made from other available starting materials (in which case such materials are intermediate compounds in the methods for making the materials of the invention).

[0051]

In addition, the methods for making the materials of the invention include, a method for forming a final compound could include Methods A, B and/or C above. For example, one organic group, preferably fluorinated, could become bound to the group 14 element M by Method A followed by binding a second organic group, preferably fluorinated, to the group 14 element M by Method B. Or, Method B could be performed first, followed by Method A - or Method C could be performed in combination with Methods A and/or B, etc. And, of course, any particular reaction (binding of an organic group to M) could be performed only once by a particular reaction, or multiple times (binding of multiple organic groups, the same or different from each other) by repeating the same reaction (a, b or c) multiple times. Many combinations of these various reactions and starting materials are possible. Furthermore, any of the methods or method combinations could include any of a number of additional steps including preparation of the starting material, replacing one or more alkoxy groups of the final compound with halogens, purifying the final compound, hydrolysis and condensation of the final compound (as will be described further below), etc.

DESCRIPTION OF PREFERRED EMBODIMENTS

[0052]

Example 1 (making a Compound I via Method B):

$$CF_2=CF-Cl + sec/tert\text{-}BuLi \rightarrow CF_2=CF-Li + BuCl$$

$$CF_2=CF-Li + Si(OEt)_4 \rightarrow CF_2=CF-Si(OEt)_3 + EtOLi$$
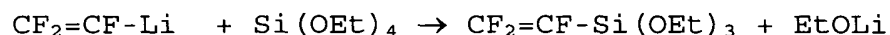
200 ml of freshly distilled dry Et_2O is added to a 500 ml vessel (under an argon atmosphere). The vessel is cooled down to -80°C and 15 g (0.129 mol) of $CF_2=CFCl$ gas is bubbled to

Et$_2$O. 100 ml (0.13 mol) of *sec*-BuLi is added dropwise during three hours. The temperature of the solution is kept below - 60°C all the time. The solution is stirred for 15 minutes and 29 ml (27.08 g, 0.130 mol) of Si(OEt)$_4$ is added in small portions. The solution is stirred for over night allowing it to warm up to room temperature. Formed red solution is filtered and evaporated to dryness to result crude trifluorovinyltriethoxysilane, CF$_2$=CFSi(OEt)$_3$.
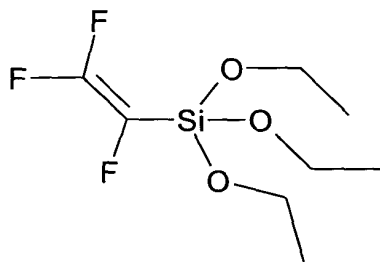
[0053]

Example 2 (making a Compound I via Method C):

   CF$_2$=CF-Li + ClSi(OEt)$_3$ → CF$_2$=CF-Si(OEt)$_3$ + LiCl
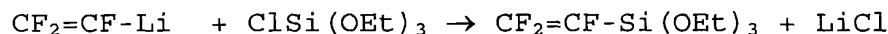
CF$_2$=CFSi(OEt)$_3$ is also formed when 30.80 g (0.155 mol) ClSi(OEt)$_3$ in Et$_2$O is slowly added to solution of CF$_2$=CF-Li (0.155 mol, 13.633g, prepared *in situ*) in Et$_2$O at -78°C. Reaction mixture is stirred overnight allowing it slowly warm to room temperature. LiCl is removed by filtration and solution evaporated to dryness to result yellow liquid, crude trifluorovinyltriethoxysilane.

[0054]

Example 3 (making a Compound IV via Method B or C):
   Follow steps in Example 1 or 2 above, followed by
   CF$_2$=CF-Si(OEt)$_3$ + excess SOCl$_2$ + py·HCl → CF$_2$=CF-SiCl$_3$ + 3
   SO$_2$ + 3 EtCl

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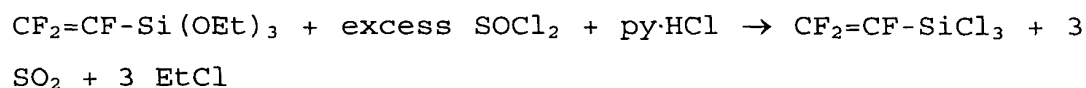
24.4 g (0.100 mol) crude trifluorovinyltriethoxysilane, 44 mL (0.60 mol, 71.4 g) thionylchloride and 1.1 g (0.0045 mol) pyridinium hydrochloride are refluxed and stirred for 24 h. Excess of SOCl$_2$ is evaporated and trifluorovinyltrichlorosilane
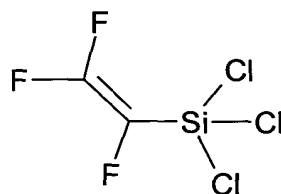
is purified by distillation.

[0055]

Example 4 (making a Compound I via Method A):

$$C_7F_7Br + Mg + excess \; Si(OEt)_4 \rightarrow C_7F_7Si(OEt)_3$$
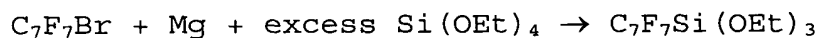
250 g (0.8418 mol) heptafluorobromotoluene, 22.69 g (0.933 mol) magnesium powder, small amount of iodine (15 crystals) and 750 mL (3.3672 mol, 701.49 g) tetraethoxysilane are mixed together at room temperature and diethylether is added dropwise to the vigorously stirred solution until an exothermic reaction is observed (~250 mL). After stirring at room temperature for 16 h diethylether is evaporated. An excess of n-heptane (~600 mL) is added to precipitate the magnesium salts. Solution is filtrated and evaporated to dryness. The residue is fractionally distilled under reduced pressure to yield heptafluorotoluene-triethoxysilane.
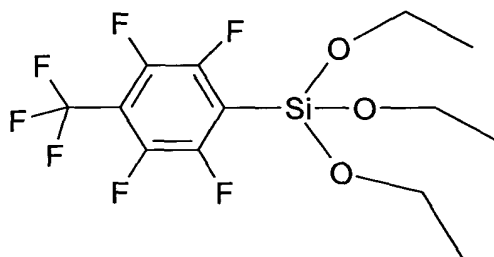
[0056]

Example 5 (making a Compound IV via Method A):

Follow the steps in Example 4, followed by

$$C_7F_7Si(OEt)_3 + 6 \ SOCl_2 + py \cdot HCl \rightarrow C_7F_7SiCl_3$$
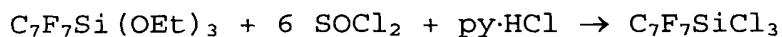
where 114.1 g (0.300 mol) heptafluorotoluenetriethoxysilane, 131 mL (1.800 mol, 214.1 g) thionylchloride and 4.51 g (0.039 mol) pyridinium hydrochloride are refluxed and stirred for 16 h. Excess of $SOCl_2$ is evaporated and perfluorotoluenetrichlorosilane
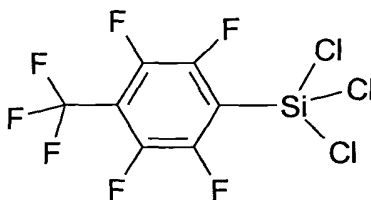
isolated by vacuum-distillation.

[0057]

Example 6 (making a Compound III via Method A):

Follow same steps as in Example 5, except isolate (by vacuum distillation at the end), perfluorotoluenedichloroethoxysilane, $CF_3-C_6F_4-Si(OEt)Cl_2$
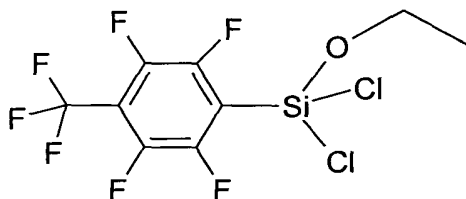
[0058]

Example 7 (making a Compound V from a Compound I or II via Method C):

1. $C_6F_5Si(OEt)_3 + SOCl_2 + py \cdot HCl \rightarrow C_6F_5Si(OEt)_2Cl + EtCl$

2. $C_6F_5Si(OEt)_2Cl + CF_2=CFLi \rightarrow C_6F_5(CF_2=CF)Si(OEt)_2$

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3. $C_6F_5(CF_2=CF)Si(OEt)_2$ + excess $SOCl_2$ + py·HCl →
 $C_6F_5(CF_2=CF)SiCl_2$
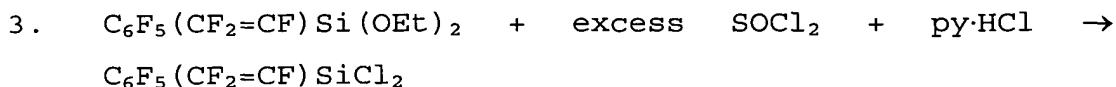
152.0 g (0.460 mol) pentafluorophenyltriethoxysilane, 34 mL (0.460 mol, 54.724 g) thionylchloride and 6.910 g (0.0598 mol) pyridinium hydrochloride are refluxed and stirred for 18 h. Pyridinium hydrochloride is precipitated at -78°C and the solution is filtrated. Pentafluorophenylchlorodiethoxysilane
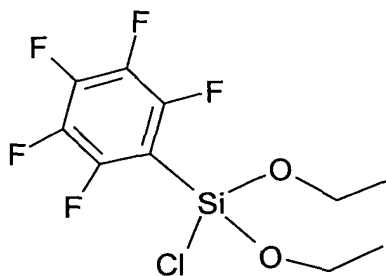
is isolated by vacuum distillation.

[0059]

Then 49.712 g (0.155 mol) pentafluorophenylchlorodiethoxysilane, $C_6F_5SiCl(OEt)_2$, in Et_2O is slowly added to solution of $CF_2=CF-Li$ (0.155 mol, 13.633g, prepared *in situ*) in Et_2O at -78°C. Reaction mixture is stirred overnight while it will slowly warm to room temperature. LiCl is removed by filtration and the product, pentafluorophenyltrifluorovinyldiethoxysilane,

purified by distillation.

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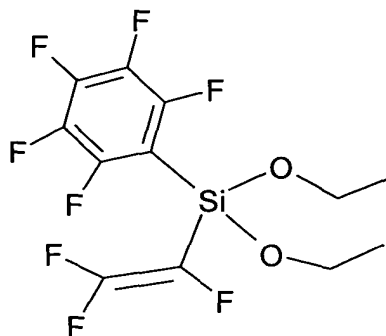
[0060]

Example 8 (making a Compound VII from a Compound I or II via Method C):

Follow the steps above for Example 7, and then 12.1 g (0.0328 mol) pentafluorophenyltrifluorovinyldiethoxysilane, 12 mL (0.1638 mol, 19.487 g) thionylchloride and 0.50 g (0.0043 mol) pyridinium hydrochloride are refluxed and stirred for 24 h. Excess of $SOCl_2$ is evaporated and residue is fractionally distilled under reduced pressure to yield a mixture of 80 % pentafluorophenyltrifluorovinyldichlorosilane.
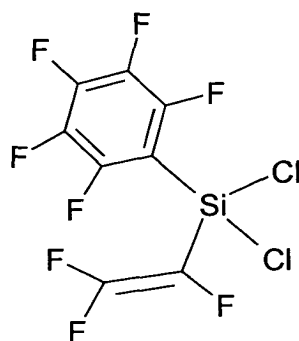
[0061]

Example 9 (making a Compound I via Method A):

$$C_6F_5Br + Mg + 2 \ Ge(OEt)_4 \rightarrow C_6F_5Ge(OEt)_3$$
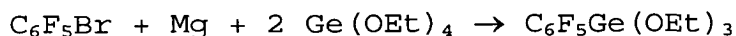
61.5 mL (0.4944 mol, 122.095 g) pentafluorobromobenzene, 13.22 g (0.5438 mol) magnesium powder and 250.00 g (0.9888 mol) tetraethoxygermane are mixed together at room temperature and diethylether is added dropwise to the vigorously stirred solution until an exothermic reaction is observed (~400 mL). After stirring at 35°C for 16 h the mixture is cooled to room temperature and diethylether evaporated. An excess of n-heptane (~400 mL) is added to precipitate the magnesium salts. Solution is filtrated and evaporated to dryness. The residue is fractionally distilled under reduced pressure to yield pentafluorophenyl-triethoxygermane.
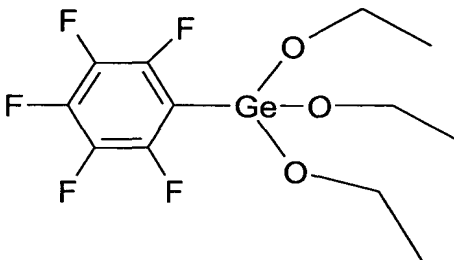
[0062]

Example 10 (making a Compound IV via Method A):

Follow the steps in Example 9, then:

50 g (0.133 mol) pentafluorophenyltriethoxygermane, 58 mL (0.80 mol, 95.2 g) thionylchloride and 1.97 g (0.017 mol) pyridinium hydrochloride are refluxed and stirred for 24 h. Excess of $SOCl_2$ is evaporated and pentafluorophenyltrichlorogermane isolated by vacuum distillation.
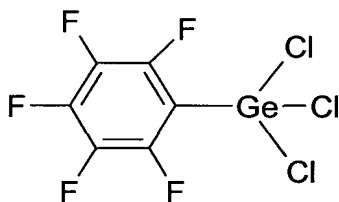

[0063]

Example 11 (making a Compound I via Method A):

$C_{10}F_7Br$ + Mg + excess $Si(OEt)_4$ → $C_{10}F_7Si(OEt)_3$
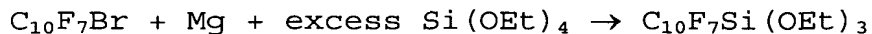
166.5 g (0.50 mol) 2-bromoperfluoronaphthalene, 13.37 g (0.55 mol) magnesium powder and 448.0 mL (2.00 mol, 416.659 g) tetraethoxysilane are mixed together at room temperature and diethylether is added dropwise to the vigorously stirred solution until an exothermic reaction is observed (~200 mL). After stirring at 35°C for 16 h the mixture is cooled to room temperature and diethylether evaporated. An excess of n-

heptane (~400 mL) is added to precipitate the magnesium salts. Solution is filtrated and evaporated to dryness. The residue is fractionally distilled under reduced pressure to yield perfluoronaphthalenetriethoxysilane.

[0064]

Example 12 (making a Compound IV via Method A):

Follow the steps in Example 11, then

100 g (0.240 mol) perfluoronaphthalenetriethoxysilane, 105.2 mL (1.442 mol, 171.55 g) thionylchloride and 3.54 g (0.0306 mol) pyridinium hydrochloride are refluxed and stirred for 24 h. Excess of $SOCl_2$ is evaporated and perfluoronaphthalenetrichlorosilane isolated by vacuum distillation.
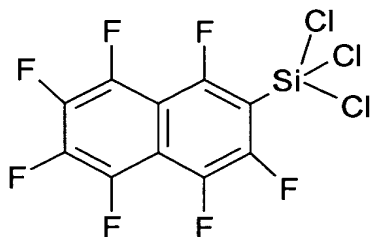
[0065]

Example 13 (making Compound V via Method A):

$$C_6F_5Br + Mg + 4\ MeSi(OMe)_3 \rightarrow C_6F_5(Me)Si(OMe)_2$$

57.9 mL (0.465 mol, 114.726 g) bromopentafluorobenzene, 12.42 g (0.511 mol) magnesium powder and 265 mL (1.858 mol, 253.128 g) methyltrimethoxysilane are mixed together at room temperature and diethylether is added dropwise to the vigorously stirred solution until an exothermic reaction is observed (~320 mL). After stirring at 45°C for 16 h the mixture is cooled to room temperature and diethylether evaporated. An excess of n-heptane (~300 mL) is added to precipitate the magnesium salts. Solution is filtrated and evaporated to dryness. The residue, methyl(pentafluorophenyl)dimethoxysilane, is used without further purification.
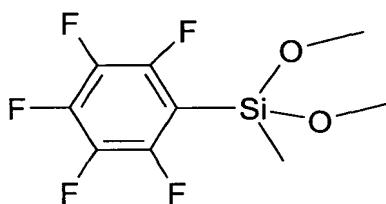
[0066]
Example 14 (Making Compound VII via Method A):

Follow steps in Example 13, then

81.68 g (0.300 mol) methyl(pentafluorophenyl)dimethoxysilane, 109 mL (1.50 mol, 178.4 g) thionylchloride and 3.69 g (0.0319 mol) pyridinium hydrochloride are refluxed and stirred for 16 h. Excess of $SOCl_2$ is evaporated and methyl(pentafluorophenyl)dichlorosilane isolated by vacuum-distillation.

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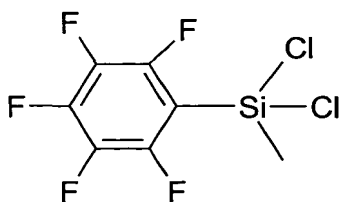
[0067]

Example 15 (making a Compound V via Method A):

$$2 \ C_6F_5Br \ + \ 2 \ Mg \ + \ Si(OEt)_4 \ \rightarrow \ (C_6F_5)_2Si(OEt)_2$$

265.2 mL (1.95 mol, 525.353 g) bromopentafluorobenzene, 52.11 g (2.144 mol) magnesium powder and 216 mL (0.975 mol, 203.025 g) tetraethoxysilane are mixed together at room temperature and diethylether is added dropwise to the vigorously stirred solution until an exothermic reaction is observed (~240 mL). The solution is stirred for 30 minutes after which additional 90 mL of Et_2O is carefully added. After stirring at 35°C for 16 h the mixture is cooled to room temperature and diethylether evaporated. An excess of n-heptane (~600 mL) is added to precipitate the magnesium salts. Solution is filtrated and evaporated to dryness. The residue is fractionally distilled under reduced pressure to yield di(pentafluorophenyl)diethoxysilane.

[0068]
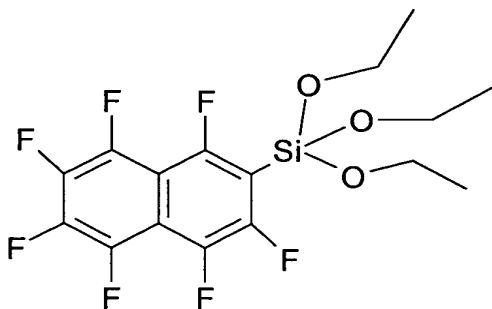
Example 16 (making a Compound V via Method C):

$$C_6F_5Cl \ + \ sec\text{-}BuLi \ \rightarrow \ C_6F_5Li \ + \ sec\text{-}BuCl$$

$$C_6F_5Li \ + \ C_6F_5Si(OEt)_2Cl \ \rightarrow \ (C_6F_5)_2Si(OEt)_2 \ + \ LiCl$$

39.52 g (0.195 mol) chloropentafluorobenzene is weighed to a 1000 mL vessel and 250 mL Et_2O is added. The vessel is

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cooled down to -70°C and 150 mL (0.195 mol) of *sec*-BuLi (1.3 M) is added dropwise during one hour. The temperature of the solution is kept below -50°C all the time. The solution is stirred for 30 minutes and 62.54 g (0.195 mol) of diethoxychloropentafluorophenylsilane in Et_2O (100 mL) is added in small portions. The solution is stirred for over night allowing it to warm up to room temperature. Formed clear solution is filtered and evaporated to dryness to result di(pentafluorophenyl)diethoxysilane, $(C_6F_5)_2Si(OEt)_2$.

[0069]
Example 17 (making a Compound VII via Method A or C):
    Follow the steps in Example 15 or Example 16, then:
    $(C_6F_5)_2Si(OEt)_2 + SOCl_2 + py\cdot HCl \rightarrow (C_6F_5)_2SiCl_2$
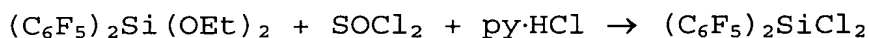
    180.93 g (0.400 mol) di(pentafluorophenyl)diethoxysilane, 146 mL (2.00 mol, 237.9 g) thionylchloride and 4.92 g (0.0426 mol) pyridinium hydrochloride are refluxed and stirred for 16 h. Excess of $SOCl_2$ is evaporated and di(pentafluorophenyl)dichlorosilane isolated by vacuum-distillation.
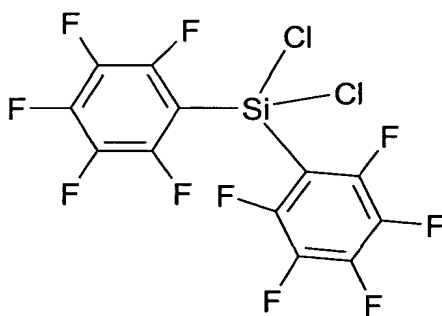

[0070]
Example 18   (making an "Other Compound" via Method A):
    $C_6F_5MgBr + HSiCl_3 \rightarrow C_6F_5(H)SiCl_2$
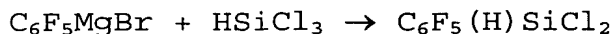
600.0 mL (0.300 mol) pentafluorophenyl magnesiumbromide (0.5 M sol. in Et_2O) is added dropwise to a solution of 30.3 mL (0.300 mol, 40.635 g) $HSiCl_3$ in Et_2O at -70°C. Reaction mixture is allowed to warm slowly to room temperature by stirring overnight. Diethylether is evaporated and an excess of n-heptane (~200 mL) is added to precipitate the magnesium salts. Solution is filtrated and evaporated to dryness. The residue, pentafluorophenyldichlorosilane, is purified by fractional distillation.
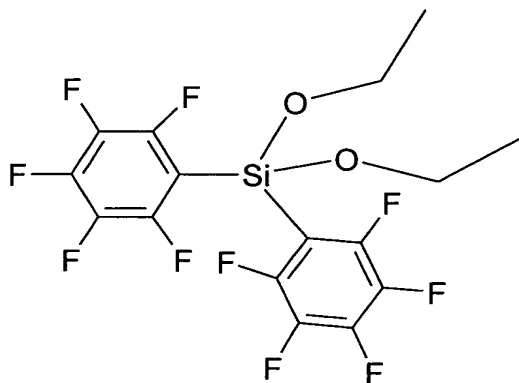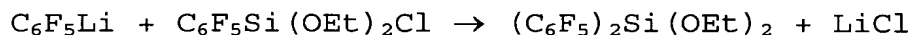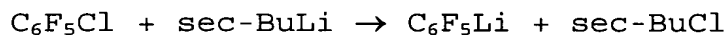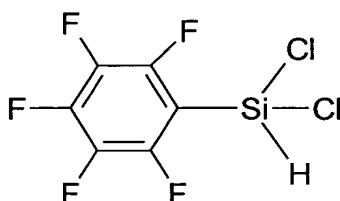

[0071]

Example 19 (making a Compound I via Method C):

$$CH\equiv C-Na + ClSi(OEt)_3 \rightarrow CH\equiv C-Si(OEt)_3 + NaCl$$
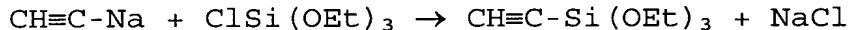
79.49 g (0.400 mol) $ClSi(OEt)_3$ in Et_2O is slowly added to a slurry of $CH\equiv C-Na$ (0.400 mol, 19.208 g) in Xylene/light mineral oil at -78°C. Reaction mixture is stirred overnight allowing it slowly warm to room temperature. NaCl is removed by filtration and solution evaporated to dryness to result acetylenetriethoxysilane.
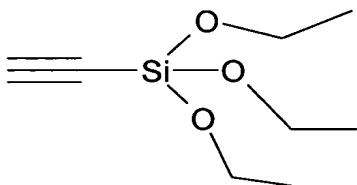
[0072]

Example 20 (making a Compound VII via Method A):

$$C_6F_5Br + Mg + CH_2=CH\text{-}Si(OEt)_3 \rightarrow C_6F_5(CH_2=CH)Si(OEt)_2$$

$$C_6F_5(CH_2=CH)Si(OEt)_2 + SOCl_2 + py\cdot HCl \rightarrow C_6F_5(CH_2=CH)SiCl_2$$
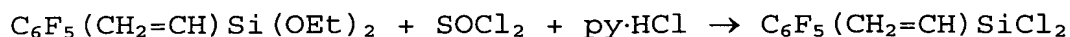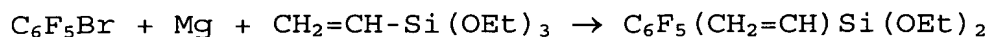
100 mL (0.8021 mol, 198.088 g) pentafluorobromobenzene, 24.90 g (1.024 mol) magnesium powder and 670 mL (3.2084 mol, 610.623 g) vinyltriethoxysilane are mixed together at room temperature and Et_2O is added dropwise to the vigorously stirred solution until an exothermic reaction is observed (~400 mL). After stirring at 35°C for 16 h the mixture is cooled to room temperature and diethylether evaporated. An excess of n-heptane (~500 mL) is added to precipitate the magnesium salts. Solution is filtrated and evaporated to dryness. The residue is fractionally distilled under reduced pressure to yield pentafluorophenylvinyldiethoxysilane.
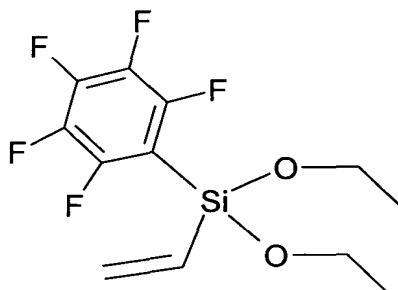
[0073]

120.275 g (0.3914 mol) pentafluorophenylvinyldiethoxysilane, 143 mL (1.9571 mol, 232.833 g) thionylchloride and 5.880 g (0.0509 mol) pyridinium hydrochloride are refluxed and stirred for 24 h. Excess of $SOCl_2$ is evaporated and pentafluorophenylvinyldichlorosilane
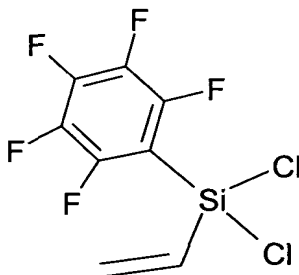
isolated by vacuum distillation.

[0074]

Example 21 (making a Compound I from Method B):

$$CH_2=CH-C(=O)-O-Na + ClSi(OEt)_3 \rightarrow CH_2=CH-C(=O)-O-Si(OEt)_3 + NaCl$$
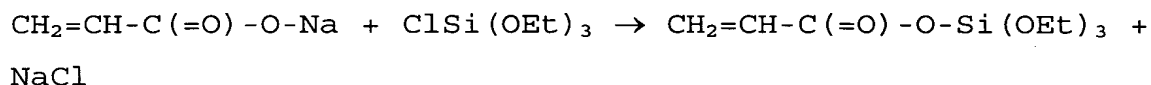
6.123 g (0.0651 mol) sodium acrylate is dissolved to 25 mL THF and cooled to -70°C. 12.8 mL (0.0651 mol, 12.938 g) chlorotriethoxysilane in THF (15 mL) is added dropwise to reaction solution. The solution is stirred for over night allowing it to warm up to room temperature. NaCl is removed by filtration and solution evaporated to dryness to result clear liquid, acryltriethoxysilane.

[0075]

Example 22 (making a Compound II):

$$CF_3-(CF_2)_7-CH_2-CH_2-Si(OEt)_3 + SOCl_2 + py \cdot HCl \rightarrow CF_3-(CF_2)_7-CH_2-CH_2-Si(OEt)_2Cl$$
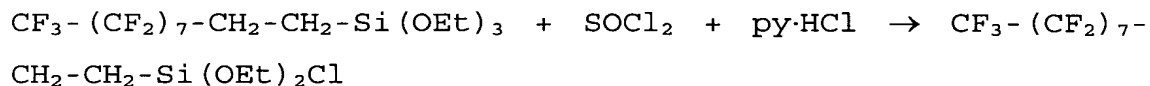
183.11 g (0.300 mol) 1H,1H,2H,2H-Perfluorodecyltriethoxysilane, 22 mL (0.300 mol, 35.69 g) thionylchloride and 4.51 g (0.039 mol) pyridinium hydrochloride are refluxed and stirred for 16 h. Excess of $SOCl_2$ is evaporated and 1H,1H,2H,2H-

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Perfluorodecylchlorodi(ethoxy)silane   isolated   by   vacuum-distillation.
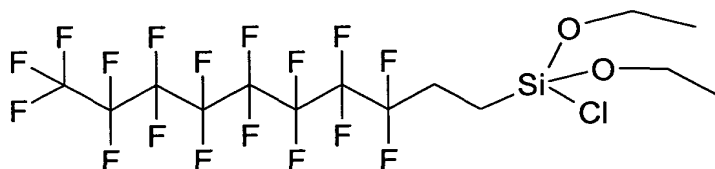
[0076]

Though this example is not using Methods A, B or C, method C could be used to add a second organic group (replacing the Cl group), or Methods A and B could be used replace an ethoxy group in the starting material with an additional organic group. Also, the starting material could be made by Methods A, B or C (starting earlier with a tetraethoxysilane and reacting as in the other examples herein).

[0077]
Example 23 (making a Compound I via Method A):

$C_8F_{17}Br + Mg + excess\ Si(OEt)_4 \rightarrow C_8F_{17}Si(OEt)_3$

$C_8F_{17}Si(OEt)_3 + excess\ SOCl_2 + py \cdot HCl \rightarrow C_8F_{17}SiCl_3$
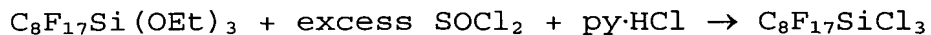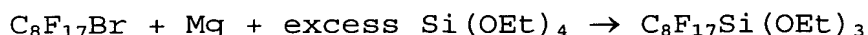
250 g (0.501 mol) 1-Bromoperfluorooctane (or 273.5 g, 0.501 mol 1-Iodoperfluorooctane), 13.39 g (0.551 mol) magnesium powder, small amount of iodine (15 crystals) and 363 mL (2.004 mol, 339.00 g) tetraethoxysilane are mixed together at room temperature and diethylether is added dropwise to the vigorously stirred solution until an exothermic reaction is observed (~200 mL). After stirring at room temperature for 16 h diethylether is evaporated. An excess of n-heptane (~400 mL) is added to precipitate the magnesium salts. Solution is filtrated and evaporated to dryness. The residue is

fractionally distilled under reduced pressure to yield perfluorooctyltriethoxysilane.
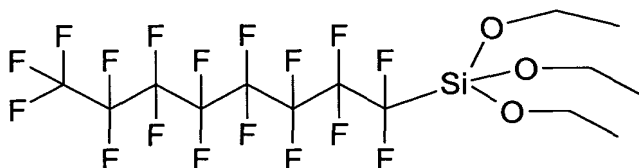
[0078]

Example 24 (making a Compound IV via Method A):

Follow the steps in Example 23, then

174.7 g (0.300 mol) perfluorooctyltriethoxysilane, 131 mL (1.800 mol, 214.1 g) thionylchloride and 4.51 g (0.039 mol) pyridinium hydrochloride are refluxed and stirred for 16 h. Excess of $SOCl_2$ is evaporated and perfluorooctyltrichlorosilane isolated by vacuum-distillation.
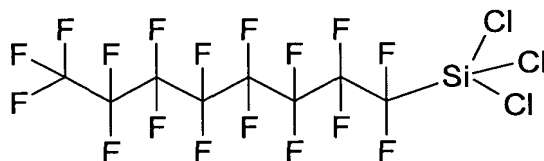
[0079]

Example 25 (making a Compound I via Method A):

$CF_2=CF-O-CF_2-CF_2-Br$ + Mg + excess $Si(OEt)_4$ → $CF_2=CF-O-CF_2-CF_2-Si(OEt)_3$
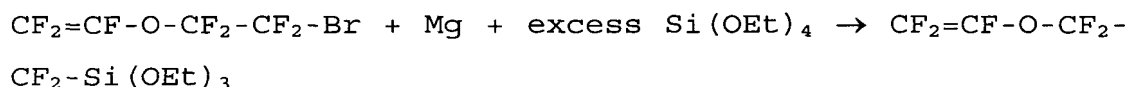
138.47 g (0.500 mol) 2-Bromotetrafluoroethyl trifluorovinyl ether, 13.37 g (0.550 mol) magnesium powder, small amount of iodine (10 crystals) and 362 mL (2.000 mol, 338.33 g) tetraethoxysilane are mixed together at room temperature and diethylether is added dropwise to the vigorously stirred solution until an exothermic reaction is observed (~200 mL). After stirring at room temperature for 16 h diethylether is evaporated. An excess of n-heptane (~400 mL) is added to precipitate the magnesium salts. Solution is

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filtrated and evaporated to dryness. The residue is fractionally distilled under reduced pressure to yield tetrafluoroethyl trifluorovinyl ether triethoxysilane.
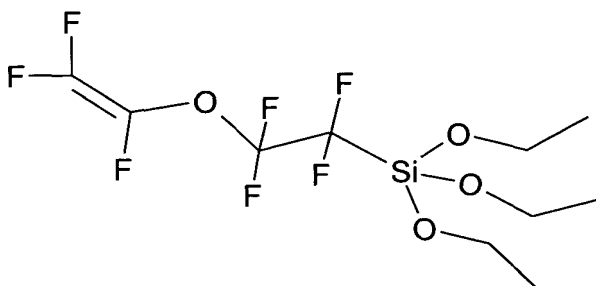

[0080]
Example 26 (making a Compound IV via Method A):

Follow steps in Example 25, followed by

108.1 g (0.300 mol) tetrafluoroethyl trifluorovinyl ether triethoxysilane, 131 mL (1.800 mol, 214.1 g) thionylchloride and 4.51 g (0.039 mol) pyridinium hydrochloride are refluxed and stirred for 16 h. Excess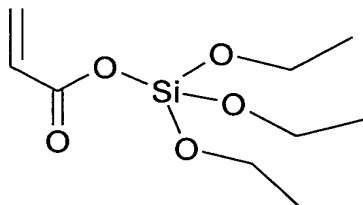 of $SOCl_2$ is evaporated and tetrafluoroethyl trifluorovinyl ether trichlorosilane is isolated by vacuum-distillation.
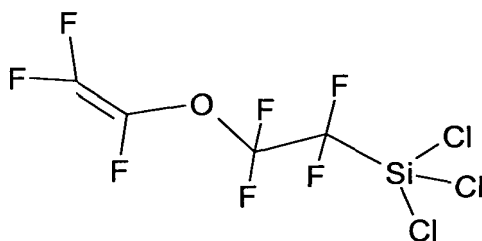
[0081]
Example 27 (making a Compound I via Method B):

$$CF \equiv C\text{-}Li + ClSi(OEt)_3 \rightarrow CF \equiv C\text{-}Si(OEt)_3 + LiCl$$

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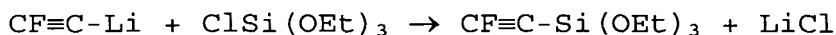
30.80 g (0.155 mol) $ClSi(OEt)_3$ in Et_2O is slowly added to solution of $CF\equiv C$-Li (0.155 mol, 7.744 g, prepared *in situ*) in Et_2O at -78°C. Reaction mixture is stirred overnight allowing it slowly warm to room temperature. LiCl is removed by filtration and solution evaporated to dryness to result fluoroacetylenetriethoxysilane.
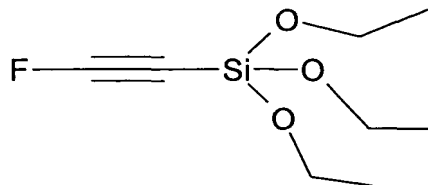

[0082]

Example 28 (making a Compound VIII via Method C):

$(C_6F_5)_2Si(OEt)_2 + SOCl_2 \rightarrow (C_6F_5)_2Si(OEt)Cl + EtCl + SO_2$

$C_6F_5Li + (C_6F_5)_2Si(OEt)Cl \rightarrow (C_6F_5)_3SiOEt + LiCl$

$(C_6F_5)_3SiOEt + SOCl_2 \rightarrow (C_6F_5)_3SiCl + EtCl + SO_2$
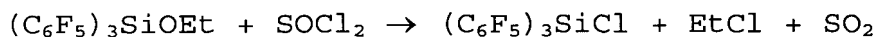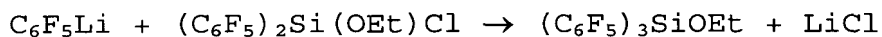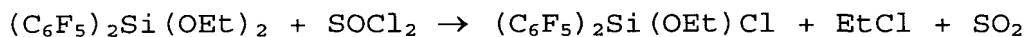
180.93 g (0.400 mol) di(pentafluorophenyl)diethoxysilane, 29 mL (0.400 mol, 47.6 g) thionylchloride and 4.92 g (0.0426 mol) pyridinium hydrochloride are refluxed and stirred for 16 h. Unreacted $SOCl_2$ is evaporated and di(pentafluorophenyl)chloroethoxysilane isolated by vacuum distillation.
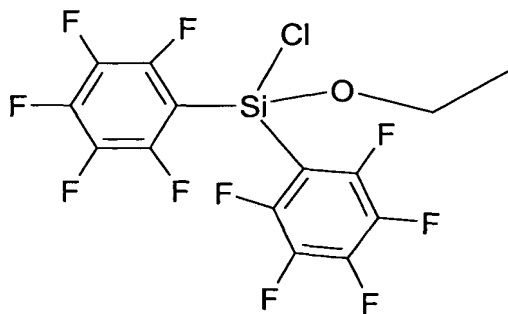
[0083]

88.54 g (0.200 mol) of di(pentafluorophenyl)chloroethoxysilane in Et₂O is slowly added to solution of C₆F₅-Li (0.200 mol, 34.80 g, prepared *in situ*) in Et₂O at -78°C. The solution is stirred for over night allowing it to warm up to room temperature. Formed clear solution is filtered and evaporated to dryness to result tri(pentafluorophenyl)ethoxysilane, (C₆F₅)₃SiOEt.
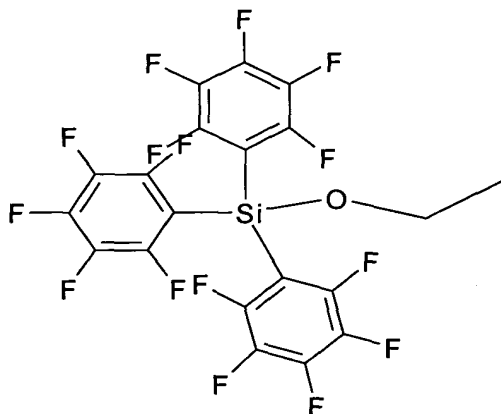
[0084]

Example 29 (making a Compound IX via Method C):

Follow steps in Example 28, followed by

114.86 g (0.200 mol) tri(pentafluorophenyl)ethoxysilane, 14.6 mL (0.200 mol, 23.8 g) thionylchloride and 2.46 g (0.0213 mol) pyridinium hydrochloride are refluxed and stirred for 16 h. Unreacted SOCl₂ is evaporated and tri(pentafluorophenyl)chlorosilane isolated by vacuum-distillation.
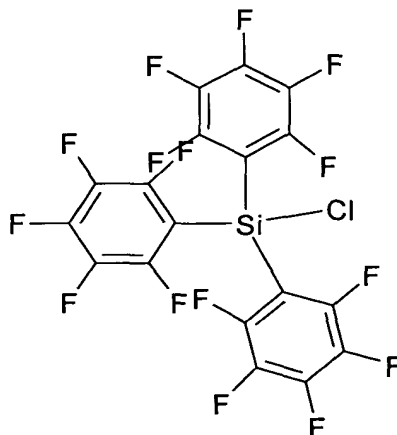
[0085]

In addition to altering the organic groups in the above examples, it is of course also possible to use other reagents in the methods above. For example, in place of diethyl ether, other solvents such as THF could be used. In place of n-heptane (in Method A) other non polar solvents such as n-hexane could be used. And in place of thionyl chloride (for replacing one or more alkoxy groups with a halogen), chlorine, hydrochloric acid, hydrobromic acid, thionylbromide, chlorine or sulfurylchloride could be used. Also, the temperatures and times (and other process parameters) can be varied as desired. In one example, it is preferred that the molar ratio of the starting material to R^2X^1 (Methods B or C) is 0.5:1 to 2:1 — preferably 1:1. Also, the starting material and R^2X^1 are preferably mixed at a temperature less than −40C degrees, e.g. between −50C and −100C and warmed to a higher temperature over a period of four hours or more (this higher temperature can be room temperature or higher if desired) − or over a longer period of time such as overnight.

[0086]

As can be seen from the examples above, Methods B and C involve reacting a first compound (having an M group selected from group 14 of the periodic table, 0, 1 or 2 organic groups bound to M) with a second compound (having an element from group 1 of the periodic table and a "new" organic group). As can also be seen from the above, such a reaction can take place if the first compound has alkoxy groups bound to M or both alkoxy and halogen groups (0, 1 or 2 halogen groups) bound to M. Method C, as mentioned earlier, is a variation of

Method B - and both methods can be viewed as comprising: reacting a compound of the general formula $R^1_{4-m}MOR^3_{m-n}X_n$, where R^1 is any nonfluorinated (including deuterated) or partially or fully fluorinated organic group (preferably a partially or fully fluorinated aryl, alkenyl, alkynyl or alkyl group) as set forth above, where M is selected from group 14 of the periodic table, where X is a halogen, where OR^3 is an alkoxy group, where m = 2 to 4 and n = 0 to 2. $R^1_{4-m}MOR^3_{m-n}X_n$ is reacted with R^2X^1 where R^2 is selected from alkyl, alkenyl, aryl or alkynyl (and where R^2 is fluorinated (fully or partially), and where X^1 is an element from group 1 of the periodic table. X^1 is preferably Na, Li or K, more preferably Na or Li, and most preferably Li. M is preferably Si, Ge or Sn, more preferably Si or Ge, and most preferably Si. X is preferably Cl, Br or I, more preferably Cl or Br, and most preferably Cl. OR^3 is preferably an alkoxy group having from 1 to 4 carbon atoms, more preferably from 1 to 3 carbons, and most preferably 2 carbons (ethoxy). Also, "m" is preferably 3 or 4, whereas "n" is preferably 0 or 1.

[0087]

R^1 and R^2 are independently preferably partially or fully fluorinated (though not necessarily as can be seen in prior examples) organic groups such as an aryl group (by aryl group we mean any organic group having a ring structure) though preferably a five or six carbon ring that is unsubstituted or substituted. For a six carbon ring structure, 1, 2 or 3 substituents can be bound to the ring, which substituents can be actively bound to the ring via a variation on the Method C set forth above (to be described further below). The substituents can be alkyl groups of any desired length, straight or branched chain, preferably fluorinated, and preferably having from 1 to 4 carbon atoms. Or the substituents on the ring structure can comprise a C=C double

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bond and be an alkenyl group (by alkenyl group we mean any organic group with a C=C double bond) such as an acrylate, vinyl or allyl group. A fluorinated vinyl, methyl or ethyl group on a fluorinated phenyl group are examples. Or, the aryl group could be a multi ring structure (e.g. perfluoronaphthalene or a biphenyl group). Or R^1 and R^2 could independently be an alkenyl group such as a vinyl or longer chain group having a C=C double bond, or a group having other types of double bonds (e.g C=O double bonds or both C=C and C=O double bonds) such as acrylate and methacrylate groups. R^1 and R^2 could also be an alkynyl group (by alkynyl group we mean any organic group with a carbon-carbon triple bond) as mentioned previously, as well as an alkyl group. If an alkyl group (by alkyl group we mean a carbon chain of any length), preferably the carbon chain is from 1 to 14, and more preferably from 4 to 8. Perfluorinated alkyl groups from 1 to 8 carbons can be used, as well as fluorinated (e.g. partially fluorinated) groups longer than 8 carbons. All the organic groups above could be deuterated in stead of fluorinated (or partially deuterated and partially fluorinated), though fully or partially fluorinated (particularly fully fluorinated) is preferred.

[0088]

In Method C set forth above, an organic (or hybrid) group "R" (e.g. R2) becomes bound to a group 3-6 or 13-16 element "M" by replacing a halogen "X" bound to "M" via the specified reaction. In an alternative to this method (Method D), an organic (or hybrid) group "R" (e.g. R1) comprises the halogen "X" - preferably Cl or Br (rather than "X" being bound to "M"). Thus when the reaction is performed, R2 replaces X bound to R1, such that R2 becomes bound to R1 (which is in turn bound to M). Preferably the other groups bound to M are alkoxy groups (OR3) or other organic groups. More

particularly, such a method comprises providing a compound $X_aR^1MOR^3{}_2R^4$ where a is from 1 to 3, X is a halogen(s) bound to R^1, R1 is an organic group (preferably an aryl, alkyl, alkenyl or alkynyl – more preferably an alkyl or aryl group), OR^3 is an alkoxy, and R^4 is either an additional alkoxy group or an additional organic group (selected from aryl, alkyl, alkenyl or alkynyl), and reacting this compound with R^2M^1 where M^1 is selected from group 1 of the periodic table and R^2 is an organic group preferably selected from aryl, alkyl, alkenyl and alkynyl, etc., so as to form $R^2{}_aR^1MOR^3{}_2R^4$.

[0089]

In one example, R^4 is an alkoxy group the same as OR^3, such that the method comprises reacting $X_aR^1MOR^3{}_3$ with R^2M^1 to form $R^2{}_aR^1MOR^3{}_3$ (where R^1 and OR^3 are bound to M and R^2 is bound to R^1. In another example, R^4 is an organic group selected from aryl, alkyl, alkenyl and alkynyl. Preferably OR^3 is a methoxy, ethoxy or propoxy, R^1 is an aryl or alkyl (straight or branched chain) having from 1 to 14 carbons, and R^2 is an aryl, alkyl, alkenyl or alkynyl, where a = 1 or 2 if R^1 is an alkyl and a = 1, 2 or 3 if R^1 is an aryl group. R^2 can be an epoxy, acrylate, methacrylate, vinyl, allyl or other group capable of cross linking when exposed to an electron beam or in the presence of a photoinitiator and electromagnetic energy (e.g. UV light).

[0090]

Example A (forming a Compound I or IV via Method D):

$1,4\text{-}Br_2C_6F_4$ + Mg + $Si(OEt)_4$ $\longrightarrow$ $Br(C_6F_4)Si(OEt)_3$

$Br(C_6F_4)Si(OEt)_3$ + $CF_2{=}CFLi$ $\longrightarrow$ $CF_2{=}CF)(C_6F_4)Si(OEt)_3$

$(CF_2{=}CF)(C_6F_4)Si(OEt)_3$ + excess $SOCl_2$ $\overset{py \cdot HCl}{\longrightarrow}$

$CF_2{=}CF)(C_6F_4)SiCl_3$
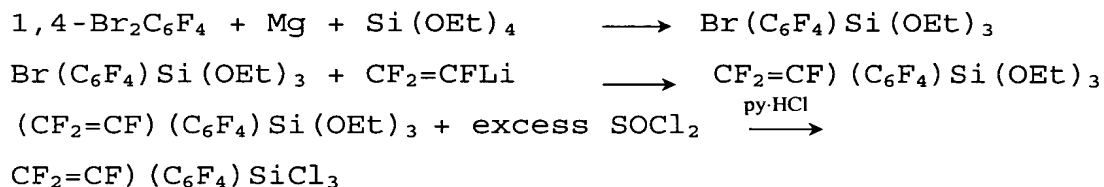
250 g (0.812 mol) 1,4-dibromotetrafluorobenzene, 21.709 g (0.8932 mol) magnesium powder, small amount of iodine (15 crystals) and 181 mL (0.812 mol, 169.164 g) tetraethoxysilane were mixed together at room temperature and diethylether was added dropwise to the vigorously stirred solution until an exothermic reaction was observed (~250 mL). After stirring at room temperature for 16 h diethylether was evaporated. An excess of n-heptane (~600 mL) was added to precipitate the magnesium salts. Solution was filtrated and evaporated to dryness. The residue was fractionally distilled under reduced pressure to yield 4-bromotetrafluorophenyltriethoxysilane.
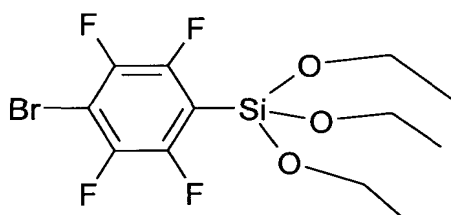
[0091]

78.246 g (0.200 mol) 4-bromotetrafluorophenyltriethoxysilane in Et_2O is slowly added to solution of $CF_2=CF-Li$ (0.200 mol, 17.592 g, prepared *in situ*) in Et_2O at -78°C. Reaction mixture is stirred overnight while it will slowly warm to room temperature. LiBr is removed by filtration and the product, 4-triethoxysilyl-perfluorostyrene, purified by distillation.
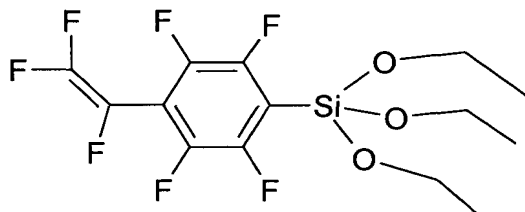
[0092]

117.704 g (0.300 mol) 4-triethoxysilylperfluorostyrene, 131 mL (1.800 mol, 214.1 g) thionylchloride and 4.51 g (0.039 mol) pyridinium hydrochloride were refluxed and stirred for 16

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h.   Excess of $SOCl_2$ was evaporated and 4-trichlorosilyl-
perfluorostyrene isolated by vacuum-distillation.
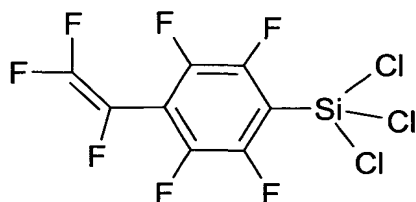
[0093]

The above example could be modified where 2 or 3 halogens
(in this case Br) are bound to the phenyl group so as to
result in multiple vinyl substituents.   Also, the phenyl group
could be another organic group such as an straight or branched
chain alkyl group, a multi ring aryl group, etc., whereas the
vinyl group could be any suitable organic group capable of
binding to a group I element (in the above example Li) and
replacing the halogen (in the above example Br).   Examples
other than vinyl include methyl, ethyl, propyl, phenyl, epoxy
and acrylate.

[0094]

Example B (forming a Compound I via Method D):

   $CF_2Cl-C(=O)-ONa$ + $ClSi(OEt)_3$ → $CF_2Cl-C(=O)-O-Si(OEt)_3$ +
   NaCl

   $CF_2=CF-Li$ + $CF_2Cl-C(=O)-O-Si(OEt)_3$ → $CF_2=CF-CF_2-C(=O)-O-$
   $Si(OEt)_3$ + LiCl
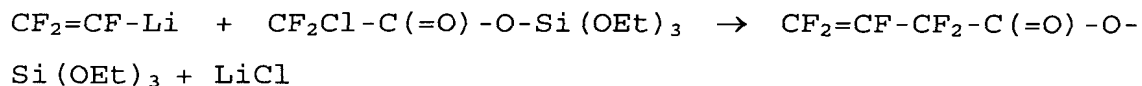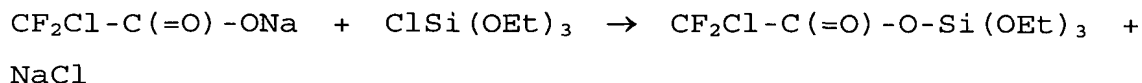
[0095]

15.246 g (0.10 mol) sodium chlorodifluoroacetate, is
dissolved to 100 mL Et_2O and cooled to -70°C. 19.7 mL (0.10
mol, 19.872 g) chlorotriethoxysilane in Et_2O (50 mL) was added
dropwise to reaction solution. The solution was stirred for
over night allowing it to warm up to room temperature. NaCl is
removed by filtration and solution evaporated to dryness to

result clear colourless liquid, chlorodifluoroacetic acid, triethoxysilyl ester.
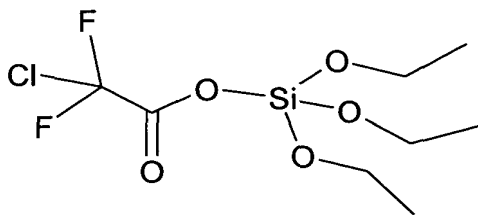
[0096]

29.27 g (0.10 mol) chlorodifluoroacetic acid, triethoxysilyl ester, is dissolved to 100 mL Et_2O and slowly added to solution of $CF_2=CF$-Li (0.10 mol, 8.796 g, prepared *in situ*) in Et_2O at -78°C. Reaction mixture is stirred overnight allowing it slowly warm to room temperature. LiCl is removed by filtration and solution evaporated to dryness to result yellow liquid, crude perfluoro-3-butene acid, triethoxysilyl ester.
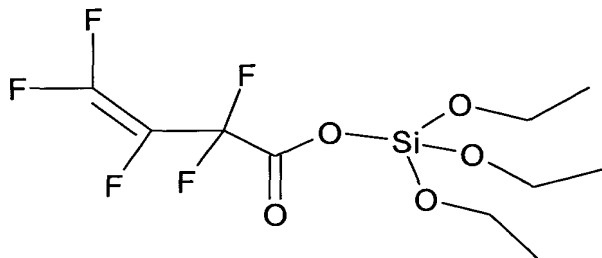
Example C (forming a Compound I or IV via Method D):

$Br(C_6F_4)Si(OEt)_3$ + C_6F_5-Li $\longrightarrow$ C_6F_5-C_6F_4-Si(OEt)$_3$ + LiBr

C_6F_5-C_6F_4-Si(OEt)$_3$ + excess $SOCl_2$ $\xrightarrow{py \cdot HCl}$ C_6F_5-C_6F_4-$SiCl_3$
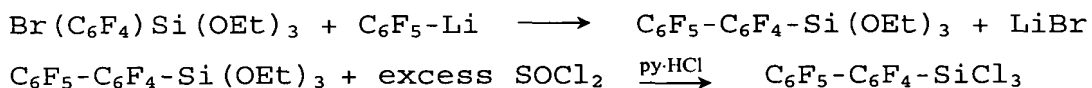
[0097]

78.246 g (0.200 mol) 4-bromotetrafluorophenyltriethoxysilane in Et_2O is slowly added

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to solution of C_6F_5-Li (0.200 mol, 34.80 g, prepared *in situ*) in Et_2O at -78°C. Reaction mixture is stirred overnight while it will slowly warm to room temperature. LiBr is removed by filtration and the product, perfluorobiphenyltriethoxysilane, purified by distillation.
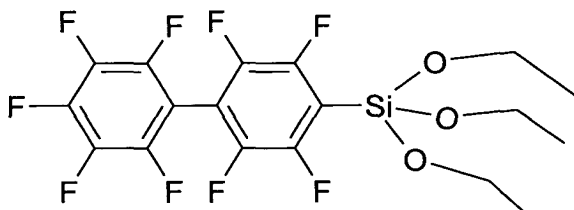
[0098]

143.516 g (0.300 mol) perfluorobiphenyltriethoxysilane, 131 mL (1.800 mol, 214.1 g) thionylchloride and 4.51 g (0.039 mol) pyridinium hydrochloride were refluxed and stirred for 16 h. Excess of $SOCl_2$ was evaporated and perfluorobiphenyltrichlorosilane isolated by vacuum-distillation.
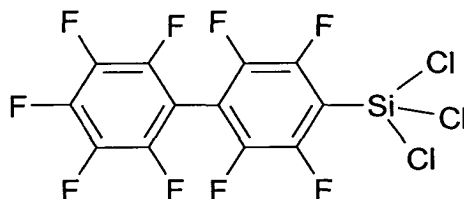
[0099]

Example D (forming a Compound I or IV via Method D):

1,4-$Br_2C_4F_8$ + Mg + Si(OEt)$_4$ $\longrightarrow$ Br(CF$_2$)$_4$Si(OEt)$_3$

Br(CF$_2$)$_4$Si(OEt)$_3$ + CF$_2$=CFLi $\longrightarrow$ CF$_2$=CF-(CF$_2$)$_4$-Si(OEt)$_3$

CF$_2$=CF-(CF$_2$)$_4$-Si(OEt)$_3$ + excess SOCl$_2$ $\xrightarrow{\text{py·HCl}}$ CF$_2$=CF-(CF$_2$)$_4$-SiCl$_3$
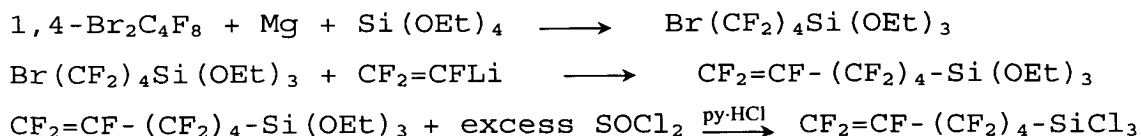
[0100]

143.94 g (0.40 mol) 1,4-dibromooctafluorobutane, 10.69 g (0.44 mol) magnesium powder, small amount of iodine (15 crystals) and 88 mL (0.40 mol, 82.42 g) tetraethoxysilane were

mixed together at room temperature and diethylether was added dropwise to the vigorously stirred solution until an exothermic reaction was observed (~200 mL). After stirring at room temperature for 16 h diethylether was evaporated. An excess of n-heptane (~400 mL) was added to precipitate the magnesium salts. Solution was filtrated and evaporated to dryness. The residue was fractionally distilled under reduced pressure to yield 4-bromooctafluorobutanetriethoxysilane.
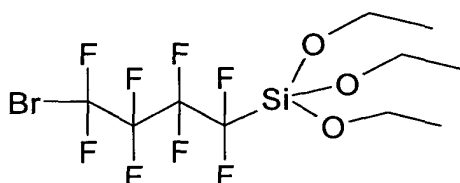

[0101]

88.641 g (0.200 mol) 4-bromooctafluorobutanetriethoxysilane in Et$_2$O is slowly added to solution of CF$_2$=CF-Li (0.200 mol, 17.592 g, prepared *in situ*) in Et$_2$O at -78°C. Reaction mixture is stirred overnight while it will slowly warm to room temperature. LiBr is removed by filtration and the product, perfluoro-1-hexenetriethoxysilane, purified by distillation.
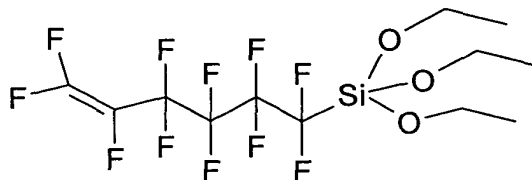
[0102]

133.295 g (0.300 mol) perfluoro-1-hexenetriethoxysilane, 131 mL (1.800 mol, 214.1 g) thionylchloride and 4.51 g (0.039 mol) pyridinium hydrochloride were refluxed and stirred for 16

h. Excess of SOCl$_2$ was evaporated and perfluoro-1-hexenetrichlorosilane isolated by vacuum-distillation.
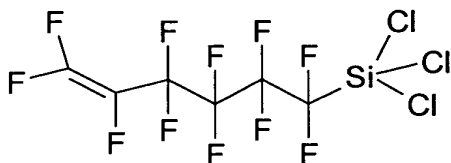
In the above "Method D" examples, R^1, R^2, R^3 and R^4 are preferably partially or fully fluorinated.

HYDROLYSIS AND CONDENSATION OF THE COMPOUND(S)

[0103]

Compounds IV, VII and IX have organic (or hybrid) R group(s) and halogen(s) (preferably Br or Cl) bound to M (selected from groups 3-6 or 13-16 – preferably group 14)). These compounds can be hydrolyzed alone or in any combination to result in a material having a –M-O-M-O- backbone with R groups bound to the backbone, and that preferably has a molecular weight of from 500 to 10,000 (more preferably from 500 to 5000). In one example, a compound selected from Compound IV is hydrolyzed with another compound selected from Compound IV. In another example, a single compound from Compound VII is hydrolyzed. Many other combinations are possible, including: a) Compound IV + Compound VII; b) Compound IV + Compound IV + Compound IV; c) Compound VII + Compound VII; d) Compound IV + Compound VII + Compound IX; e) Compound IV + Compound IV + Compound IX; f) Compound VII + Compound IX, etc. Any other combinations, in any desired ratio, can be used for the hydrolysis and eventual deposition.

[0104]

The hydrolysis/condensation procedure can comprise five sequential stages: Dissolvement, hydrolysis and co-condensation, neutralization, condensation and stabilization.

Not all stages are necessary in all cases. In the hydrolysis, chlorine atoms are replaced with hydroxyl groups in the silane molecule. The following description takes as an example compounds that have chlorine as the halogen that takes part in the hydrolysis reaction, and silicon is the metal in the compound. Hydrochloric acid formed in the hydrolysis is removed in the neutralization stage. Silanols formed in the hydrolysis are attached together for a suitable oligomer in the condensation stage. The oligomer formed in the condensation are stabilized in the end. Each stage can be done with several different ways.

[0105]
Example I:

Dissolvement. Chlorosilanes are mixed together in an appropriate reaction container and the mixture is dissolved into a suitable solvent like tetrahydrofuran. Instead of tetrahydrofuran, other solvents can be used (pure or as a mixture): acetone, chloroform, diethyl ether, ethyl acetate, methyl-isobutyl ketone, methyl ethyl ketone, acetonitrile, ethylene glycol dimethyl ether, triethylamine, formic acid, nitromethane, 1,4-dioxan, pyridine, acetic acid.

[0106]

Hydrolysis. The reaction mixture is cooled to 0 °C. The hydrolysis is performed by adding water (H_2O) into the reaction mixture. The water is added in 1:4 (volume/volume) water-tetrahydrofuran -solution. Water is used equimolar amount as there are chlorine atoms in the starting reagents. The reaction mixture is held at 0 °C temperature during the addition. The reaction mixture is stirred at room temperature for 1 hour after addition. Instead of tetrahydrofuran, water can be dissolved into pure or mixture of following solvents: acetone, chloroform, diethyl ether, ethyl acetate, methyl-

isobutyl ketone, methyl ethyl ketone, acetonitrile, ethylene glycol dimethyl ether, triethylamine, formic acid, nitromethane, 1,4-dioxan, pyridine, acetic acid. In the place of water (H_2O) can be used: deuterium oxide (D_2O) or HDO. A part of the water can be replaced with alcohols, deuterium alcohols, fluorinated alcohols, chlorinated alcohols, fluorinated deuterated alcohols, and/or chlorinated deuterated alcohols. The reaction mixture may be adjusted to any appropriate temperature. Excess of water can be used. Some level co-condensation can happen during the hydrolysis that can be seen as increment of material molecular mass.

[0107]

Neutralization. The reaction mixture is neutralized with pure sodium hydrogen carbonate. $NaHCO_3$ is added into cooled reaction mixture at 0 °C temperature ($NaHCO_3$ is added equimolar amount as there is hydrochloric acid in the reaction mixture). The mixture is stirred at the room temperature for a while. After the pH of the reaction mixture has reached value 7, the mixture is filtered. The solvent is then evaporated with rotary evaporator (p = 250 – 50 mbar, t(bath) = + 30 °C).

[0108]

Instead of $NaHCO_3$ can be used pure potassium hydrogen carbonate ($KHCO_3$), sodium carbonate (Na_2CO_3), potassium carbonate (K_2CO_3), sodium hydroxide (NaOH), potassium hydroxide (KOH), calcium hydroxide ($Ca(OH)_2$), magnesium hydroxide ($Mg(OH)_2$) ammonia (NH_3), trialkylamines (R_3N, where R is hydrogen or straight / branched chain C_xH_y, x < 10, for example triethanolamine), trialkyl ammonium hydroxides (R_3NOH, R_3N, where R is hydrogen or straight / branched chain C_xH_y, x < 10). All neutralization reagents can be added into the reaction mixture also as a solution of any appropriate solvent.

Neutralization can be performed also with solvent-solvent - extraction or with azeotropic water evaporation.

[0109]

Procedure for solvent-solvent-extraction: The solvent is evaporated off after the hydrolysis. The material is dissolved into pure or mixture of solvents such as: chloroform, ethyl acetate, diethyl ether, di-isopropyl ether, dichloromethane, methyl-isobutyl ketone, toluene, carbon disulphide, carbon tetrachloride, benzene, nitromethane, mehylcyclohexane, or chlorobenzene. The solution is extracted several times with water or D_2O until the pH of the organic layer is over value 6. The solvent is then evaporated with rotary evaporator (p = 250 - 50 mbar, t(bath) = + 30 °C).

[0110]

Procedure for azeotropic water evaporation: The solvent is evaporated off after the hydrolysis. The material is dissolved into mixture of water and one of the following solvents (1:10 volume/volume): tetrahydrofuran, ethanol, acetonitrile, 2-propanol, tert-butanol, ethylene glycol dimethyl ether, triethylamine, 2-propanol. The formed solution is evaporated to dryness. The material is dissolved again into the same mixture of water and the solvent. Evaporation and addition cycle is repeated until pH value of the material solution is 7. The solvent is then evaporated with rotary evaporator (p = 250 - 50 mbar, t(bath) = + 30 °C).

[0111]

Neutralization stage in cases where condensation stage is passed: In the neutralization stage evaporation of the solvent in the end is not necessary always. In these cases this stage is aborted after filtering (the reaction mixture is neutral)

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and the synthesis is continued in stabilization stage (the condensation stage is passed).

[0112]

Condensation. The material is stirred with magnetic stirrer bar under 12 mbar pressure for few hours. Water, which forms during this final condensation, evaporates off. The pressure in this stage can be in a large range. The material can be heated while vacuum treatment. In some cases this stage is not necessary.

[0113]

Stabilization. The material is dissolved into cyclohexanone, which is added 30 weight-% of the materials weight. The pH of the solution is adjusted to value 2,0 with acetic acid. In the place of cyclohexanone can be used any of a number of other solvents, (alone or as a mixture), such as methyl-isobutyl ketone, 2-propanol, ethanol, methanol, 1-propanol, tetrahydrofuran, acetone, nitromethane, chlorobenzene, dibutyl ether, mesitylene, 1,1,2,2-tetrachloroethane, trichloroethanes, ethyl lactate, 1,2-propanediol monomethyl ether acetate and/or carbon tetrachloride. In the place of acetic acid can be used regular or deuterated forms of following acids, among others: formic acid, propanoic acid, monofluoro acetic acid, trifluoro acetic acid, trichloro acetic acid, dichloro acetic acid and/or monobromo acetic acid.

[0114]

Stabilization in cases when the condensation stage is bypassed: Acetic acid is added into the mixture until a pH value of 3-4 is reached. The solution is evaporated until appropriate concentration of the oligomer in the solution has reached (about 50 w-% oligomer, 49 w-% solvent and 1 w-% acid,

"solvent" is the solvent of the dissolvement and hydrolysis stages).

[0115]

In Example I above, "chlorosilanes" are initially mixed together with tetrahydrofuran. As mentioned earlier, this can be an almost unlimited number and type of compounds as disclosed in detail earlier herein – including a large number of chlorosilanes and other halo-metal-organic compounds in accordance with the invention and in accordance with the ultimate properties desired in the final material. If one of the compounds to be hydrolyzed and condensed is pentafluorophenyltrichlorosilane, this can be prepared as in the methods set forth above, by:

$$C_6F_5Br + Mg + excess\ Si(OEt)_4 \rightarrow C_6F_5Si(OEt)_3 + (C_6F_5)_2Si(OEt)_2$$

$$C_6F_5Si(OEt)_3 + SOCl_2 + py \cdot HCl \rightarrow C_6F_5SiCl_3$$
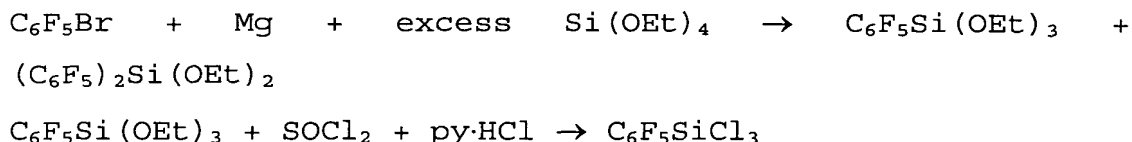
[0116]

100 mL (0.8021 mol, 198.088 g) pentafluorobromobenzene, 24.90 g (1.024 mol) magnesium powder and 716 mL (3.2084 mol, 668.403 g) tetraethoxysilane are mixed together at room temperature and diethylether is added dropwise to the vigorously stirred solution until an exothermic reaction is observed (~200 mL). After stirring at 35°C for 16 h the mixture is cooled to room temperature and diethylether evaporated. An excess of n-heptane (~500 mL) is added to precipitate the magnesium salts. Solution is filtrated and evaporated to dryness. The residue is fractionally distilled under reduced pressure to yield pentafluorophenyltriethoxysilane.
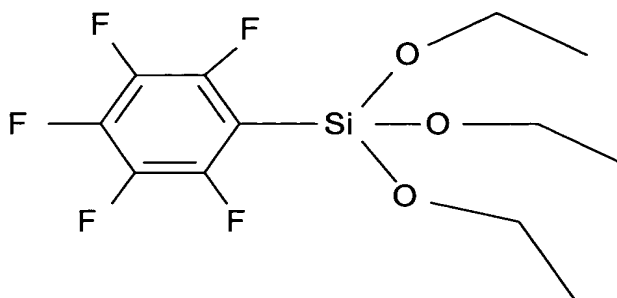
[0117]

100 mL (0.375 mol, 124.0 g) pentafluorophenyltriethoxysilane, 167 mL (2.29 mol, 272.0 g) thionylchloride and 5.63 g (0.0487 mol) pyridinium hydrochloride are refluxed and stirred for 24 h. Excess of $SOCl_2$ is evaporated and pentafluorophenyltrichlorosilane
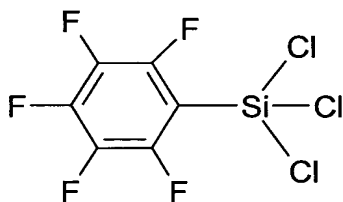
isolated by vacuum-distillation.

[0118]

If a second of the compounds to be hydrolyzed and condensed is trifluorovinyltrichlorosilane, this can be prepared by:

119 mL (0.155 mol) sec-butyllithium (1.3 M solution in cyclohexane) is added under argon with stirring to 18.053 g (0.155 mol) chlorotrifluoroethylene

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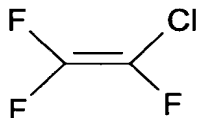
dissolved in Et$_2$O at -80°C. After the addition is complete the reaction mixture is stirred for 15 min to yield lithiumtrifluoroethylene.

$$\begin{array}{c}F \\ \diagdown \\ \diagup \\ F\end{array} = \begin{array}{c}Li \\ \diagup \\ \diagdown \\ F\end{array}$$
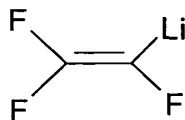
[0119]

30.80 g (0.155 mol) ClSi(OEt)$_3$ in Et$_2$O is slowly added to solution of CF$_2$=CF-Li (0.155 mol, 13.633g, prepared *in situ*) in Et$_2$O at -78°C. Reaction mixture is stirred overnight while it will slowly warm to room temperature. LiCl is removed by filtration and the product, trifluorovinyltriethoxysilane,
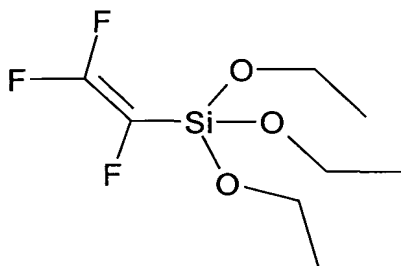
is isolated by distillation.

[0120]

24.4 g (0.100 mol) trifluorovinyltriethoxysilane, 44 mL (0.60 mol, 71.4 g) thionylchloride and 0.497 g (0.0045 mol) pyridinium hydrochloride are refluxed and stirred for 24 h. Excess of SOCl$_2$ is evaporated and trifluorovinyltrichlorosilane
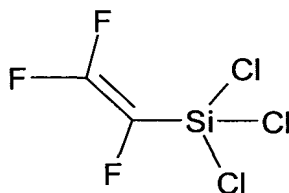
is purified by distillation.

[0121]

Then, to a solution of trifluorovinyltrichlorosilane and pentafluorophenyltrichlorosilane at a molar ratio 1:1 in dehydrated tetrahydrofuran, is added dropwise a stoichiometric amount of water (e.g. H2O or D2O) in THF at 0°C (nonstoichiometric amounts, higher or lower, can also be used). After stirring for 1 hour, the solution is neutralized with 3 equivalents of sodium hydrogencarbonate. After confirming the completion of generation of carbonic acid gas from the reaction solution, the solution is filtered and volatile compounds are removed by vacuum evaporation to obtain colorless, transparent viscous liquid, poly(pentafluorophenyltrifluorovinyl-siloxane), in a three dimensional network of alternating silicon and oxygen atoms.

[0122]

Figure 1 is an example of a method comprising: reacting a compound of the general formula R1MX3$_3$ with a compound of the general formula R2MX3$_3$ where R1 is selected from alkyl, alkenyl, aryl and alkynyl, R2 is selected from alkenyl, aryl or alkynyl, M is an element selected from groups 3-6 or 13-16 though preferably from group 14 of the periodic table, and X3 is a halogen; with H2O or D2O; so as to form a compound having a molecular weight of from 500 to 10,000 with a -M-O-M-O- backbone with R1 and R2 substituents on each M. In the hydrolysis example above, silicon atoms of the network are modified by pentafluorophenyl and trifluorovinyl groups in an approximate ratio 1:1. Of course other ratios are possible depending upon the ratio of starting materials, and, of course, other three dimensional networks can be achieved by having other (or additional) starting materials selected from Compound IV, VII and IX, along with other hydrolyzable materials. An alternate example is a method comprising: reacting a compound of the general formula R1R2MX3$_2$ where R1

is selected from alkyl, alkenyl, aryl and alkynyl, R2 is selected from alkenyl, aryl or alkynyl, M is an element selected from group 14 of the periodic table, and X3 is a halogen; with D2O; so as to form a compound having a molecular weight of from 500 to 10,000 with a -M-O-M-O- backbone with R1 and R2 substituents on each M. As mentioned above, Compounds IV, VII and IX have organic (or hybrid) R group(s) and halogen(s) (preferably Br or Cl) bound to M (selected from groups 3-6 or 13-16 – preferably group 14)) and can be combined in almost limitless combinations – e.g. a compound selected from the Compound IV group could be hydrolyzed with another compound selected from Compound IV. In another example, a single compound from Compound VII is hydrolyzed. Many other combinations are possible, including: Compound IV + Compound VII; Compound IV + Compound IV + Compound IV; Compound VII + Compound VII; Compound IV + Compound VII + Compound IX; Compound IV + Compound IV + Compound IX; Compound VII + Compound IX, etc. – which various combinations of compounds will result in a hydrolyzed material having at least one organic substituent bound to an inorganic oxide backbone – preferably from 2 to 6 different organic substituents bound to the backbone prior to deposition and exposure. The presence of the organic groups, preferably all fluorinated, allows for improved optical absorption characteristics due to minimal or absent C-H bonds in the deposited material (preferably the hydrolyzed/condensed material has a hydrogen content of 10% or less, preferably 5% or less, and more preferably 1% or less).

[0123]

Also, though "M" in the above hydrolysis example is silicon, it is possible to have materials with other M groups, or "dope" one or more silanes to be hydrolyzed with a lesser (though not necessarily lesser) amount of a compound having a

different M group such as boron, a metalloid and/or an early transition metal (e.g. B, Al, Si, Ge, Sn, Sb, Pb, Ta, Ti, Zr, Er, Yb and/or Nb). As an example, a material could be formed from hydrolyzing/condensing one or more compounds each formed of silicon, chlorine and one or more fluorinated organic compounds bound to the silicon, whereas another material could be formed by hydrolyzing/condensing such compound with one or more additional compounds that each comprise an element other than silicon (Ge, Nb, Yb etc.), chlorine and one or more fluorinated organic groups. In this way, the inorganic backbone of the hydrolyzed/condensed material will comprise silicon, oxygen and the element(s) other than silicon, with fluorinated organic groups bound to this backbone.

DEPOSITION OF THE HYDROLYZED AND CONDENSED MATERIAL
[0124]

The material formed as above preferably has a molecular weight between 500 and 10,000, more preferably between 500 and 5000. Other molecular weights are possible within the scope of the invention, however a weight between 500 and 5000 provides the best properties for depositing the material on a substrate. The substrate can be any suitable substrate, such as any article of manufacture that could benefit from the combined benefits of a hybrid organic-inorganic material as an adhesion promoter. In general, the siloxane oligomer – the hybrid organic-inorganic material having the molecular weight as set forth above -- is mixed with a suitable solvent and deposited. The solvent can be any suitable solvent, such as isopropanol, ethanol, methanol, THF, mesitylene, toluene, cyclohexanone, cyclopentanone, dioxane, methyl isobutyl ketone, or perfluorinated toluene. Generally, adhesion promoters are used as dilute solutions to cover the substrate without any wetting problems.

[0125]

Deposition is generally at a temperature of 200C or less (can be at 150C or less). If the material is annealed after deposition, it is preferably at 200C or less. If the material is to be patterned by exposure to electromagnetic radiation (e.g. UV light) then a photoinitiator can be mixed into the material along with the solvent. There are many suitable types of photoinitiators that could be used, such as Irgacure 184, Irgacure 500, Irgacure 784, Irgacure 819, Irgacure 1300, Irgacure 1800, Darocure 1173 or Darocure 4265. The initiator could be highly fluorinated, such as 1,4-bis(pentafluorobenzoyl)benzene or Rhodosil 2074 photoinitiator. Also, thermal initiators can be applied for thermal crosslinking of organic carbon double bond moieties, such as with Benzoyl peroxide, 2,2'- Azobisisobutyronitrile, or tert-Butyl hydroperoxide. The amount of these photo or thermal initiators may vary from 0.1 to 5 w-%. They may appear in solid or liquid phase. The initiator is carefully mixed with the material that already contains "processing solvent". (Organic dopants or liquid crystal dopants – or erbium -- can be mixed with the material at this point if desired.) Finally the material is filtered through inert semiconductor grade filter to remove all undissolved material.

[0126]

Spin-on processing. After hydrolysis and condensation, the material solution is deposited on a substrate in a spin-on process (or by dipping, spray and meniscus coating, etc.). Both static and dynamic deposition can be used. The material is first spread over a wafer or other substrate at low speed (50 to 700 rpm) for 5 to 10 seconds and then the speed is increased by 500 to 5000 rpm/s acceleration to about 5000 rpm depending upon starting speed. However, slower speeds may be used if very thick films are required. If 1000 rpm spinning

speed is applied film thicknesses from 100 nm to 30,000 nm are achieved depending on material viscosity. Material viscosity can be tuned by increasing the amount of process solvent, which typically have relative low vapor pressure and high boiling point. Spinning is continued for 30 to 60 seconds to obtain uniform film over the wafer.

[0127]

The substrate can be any suitable substrate or article. In many cases, the substrate will be a planar wafer-type substrate, such as a glass, plastic, quartz, sapphire, ceramic or a semiconductor substrate (e.g. germanium or silicon). The substrate can have electronic or photonic circuitry thereon. For example, the substrate could be an integrated circuit or a printed circuit board.

[0128]

There is essentially no limit to the number or types of photonic or electronic devices that could be integrated with the deposited material.

[0129]

Deposition Example 1:

Equal (molar) amounts of vinyl trichlorosilane and phenyl trichlorosilane are measured into a flask glass, which contains THF as a synthesis solvent. The chlorate moieties are hydrolyzed by adding stoichiometric amount of water in THF solution to the flask. During this stage the flask is kept in ice bath. The hydrolysis and co-condensation are carried out for 2 hours and then the solution is neutralized by using sodium hydro carbonate, ammonia gas or solvent extraction techniques. The solution is filtered and volatile components (mainly THF and water) are removed by vacuum evaporation. Resulting viscous solution is diluted to a solvent such as

MIBK with a ratio of 1:100 (methyl isobutyl ketone) and 1-5 % of photoinitiator is added if photosensitivity is desired property. Finally, the solution is filtered through 0.1 um PTFE filter to remove residuals and particles.

[0130]

Processing:

The prepared solution is spun-on a buffer layer by applying 4000 rpm spinning speed and dynamic deposition. The film is spin dried for 60 seconds resulting in a thin 1 nm to 100 nm film. The upper photosensitive layer (actual optical core layer) is instantly deposited on top of the dried adhesion promoter film. Both films are co-dried at 90 Celsius for 90 seconds after which they are exposed with UV-light through a contact mask or with stepper tool. Both films are developed by soaking them in a development bath. Unexposed parts are removed in the development step and a good residual free channel waveguide structure is achieved. Buffer surface is also clean and free of core development residuals.

[0131]

The above example is in relation to an adhesion promoter for forming a waveguide, however, the adhesion promoter can be used in a CMOS process, such as for increasing adhesion of a dielectric, for increasing adhesion of a passivation layer, or any layer such as one of a material that has adhesion problems (such as due to high hydrophobicity from fluorine or other groups in the material).

MATERIAL CHARACTERISTICS

[0132]

Material processed and formed on a substrate as above, was tested to determine various characteristics of the deposited and cross linked material. As will be seen below,

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some tests were performed on the material in "bulk form" –
e.g. by testing deposited material on a substrate. For
example, in testing contact angle, a bulk measurement was made
after forming a layer on a substrate. In a test of the
hydrophobicity of the hybrid material, a water contact angle
measurement can be measured. The phenomenon of wetting or
non-wetting of a solid by a liquid can be understood in terms
of the contact angle. A drop of a liquid resting on a solid
surface forming an angle relative to the surface may be
considered as resting in equilibrium by balancing the three
forces involved (namely, the interfacial tensions between
solid and liquid, that between solid and vapor and that
between liquid and vapor). The angle within the liquid phase
is known the contact angle or wetting angle. It is the angle
included between the tangent plane to the surface of the
liquid and the tangent plane to the surface of the solid, at
any point along their line of contact. The surface tension of
the solid will favor spreading of the liquid, but this is
opposed by the solid-liquid interfacial tension and the vector
of the surface tension of the liquid in the plane of the solid
surface.

[0133]

In the present invention, contact angles of 90 degrees or
more, and generally 100 degrees or more are easily achieved
(from 50 ul of ultrapure water). Depending upon the compounds
selected for hydrolysis/condensation, water contact angles of
125 degrees or more, or even 150 degrees or more can be
achieved. Particularly if all organic groups, including those
that provide bulk to the final material (e.g. a longer alkyl
chain or a single or multi ring aryl group) as well as those
that allow for cross linking (e.g. organic groups with
unsaturated double bonds), are fully fluorinated – then the
resulting material can be highly hydrophobic and result in

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very large contact angles. The hydrophobicity can easily be tailored depending upon which compounds are selected, and in what amounts, for hydrolysis/condensation.

[0134]

The optical loss of the materials were also tested and determined to be less than 0.1 dB/cm at 1550 nm. The optical loss can be less than 0.09 dB/cm (or even less than 0.075 dB/cm or less than 0.05 dB/cm) at 1550 nm, depending upon which compounds and in what amounts are selected for hydrolysis/condensation, and in particular the level of fluorination of the compounds selected. The deposited materials tested also have an optical loss less than 0.1 dB/cm (or even less than 0.075 dB/cm) at 1310 nm, C Band and L Band. The optical bulk loss measurement was carried out from bulk sample of the optical material by using Varian Gary 5 UV-Vis-IR spectrophotometer.

[0135]

The materials of the invention can be deposited as very thin layers (as thin as from 1 to 10 molecular layers), or in thicker films from 1nm up to 100 um (or more). Generally, the material is deposited at a thickness of from 0.5 to 50 um, preferably from 1 to 20 um – though of course the thickness depends upon the actual use of the material (waveguide, passivation coating, adhesive, etc.). The thickness of the deposited layer can be controlled by controlling the material viscosity, solvent content and spinning speed (if deposited by spin on). Material thickness can also be controlled by adjusting the deposition temperature of both the deposition solution and the spinner (if spin on deposition). Also, adjusting the solvent vapor pressure and boiling point by selection of solvent can affect the thickness of the deposited material. Spin on deposition can be performed on a Karl Suss

Cyrset enhanced RC8 spinner. Spray coating, dip-coating, meniscus coating, screen printing and "doctor blade" methods can also be used to achieve films of varying thickness.

[0136]

This invention has been described in connection with the preferred embodiments. Many variations of the above embodiments are contemplated as being within the scope of the invention.

ADVANTAGES OF THE INVENTION

[0137]

Adhesion promoter materials, which surface energies can be adjusted with novel precursors. The surface energy effectively changes the wetting/adhesion behaviour between the substrate and next deposited layer. Through these adjustable properties various type of materials including polymer, fluorinated polymers, metal or metalloid oxide or their fluorinated derivatives can be deposited on electrical or opto-electrical surfaces. The actual adjustment of the surface energy happens with an organic functional group or moiety attached to silicon through a covalent bond. Silicon may have 1 to 4 functional groups but more preferably 1 functional group. Silicon may also have maximum of 3 hydrolysable and condensable groups.

[0138]

Adhesion promoter material that works as a planarizing bonding or wetting layer between electrical or opto-electronics substrate and a layer deposited on top of it. Electrical or opto-electronic substrate may contain some topographic structures. The planarization property will improve the surface quality, uniformity and planarity of the deposited layer.

[0139]

Organic functional groups can be selected so that the organic group can undergo radiation induced (UV, DUV, electron radiation) polymerisation reaction with or without initiator. This makes material lithographically patternable that enables selective deposition of the adhesion promoter.

[0140]

Adhesion layer also acts as a protection layer against diffusion (such water, solvents, basis and acids) while top layer is deposited on the substrate.

[0141]

The functional organic groups can be selected so that its optical properties are adjust to match or mismatch with substrate and/or deposited layer. Therefore, the adhesion layer acts for example anti-reflection coating or it is optically invisible interface layer.

[0142]

Plasma selective removal of functional groups to modify surface energy of the adhesion promoter layer. 1 or more organic moieties can be selected so that they are easily removable by plasma treatment (argon, oxygen, nitrogen etc.) while other functional groups remain unreacted.